Studies on immobilized polymer-bound imidazole copper(II) complexes as catalysts

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STUDIES ON IMMOBILIZED POLYMER-BOUND IMIDAZOLE COPPER(II) COMPLEXES AS CATALYSTS

Wei Chen

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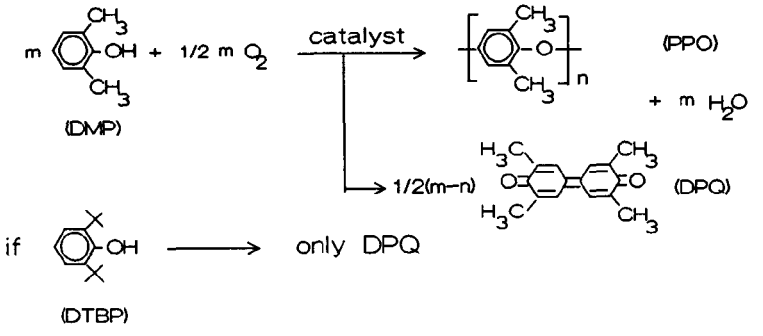
Contents

Chapter 1

Introduction

Since Merrifield introduced the concept of solid phase peptide synthesis on a cross-linked polymer in 1963 [1], a significant progress in the field of polymer-bound catalysts has been made [2-4], e.g. in polymer supported metal complex catalysts [5-9,19], optically active polymer as catalysts [10], polymeric phase transfer catalysts [11]. The practical advantages using polymer supported catalysts involve simplified reaction work-up, possibly recycling or continuous use of catalysts, the reduced contamination of products and environment, etc. [12,13]. In addition, the development in polymer-bound catalysis was also promoted by an increasing awareness of the possible influence of the polymer itself on the catalyzed reactions. This involves the so-called "macromolecular effects", such as local concentration effects, micro-environmental effects, polymer chain effects, etc. [13,14].

On the other hand, oxidative coupling polymerization of 2,6-dimethylphenol (DMP) catalyzed by copper-amine complexes under mild conditions (Scheme 1) continues to receive a great deal of attention in the last decades [15-22] because of its significant industrial importance [22]. However, the mechanism of this polymerization reaction is not yet fully understood and different views on the mechanism still exist [23].



Scheme 1

In the Laboratory of Polymer Chemistry of Groningen University the synthesis of polymer-bound copper-amine complexes as catalysts for oxidative

coupling (polymerization) of 2,6-disubstituted phenols and the mechanism of this reaction have been intensively investigated [23-27]. Particularly, immobilization of polymer-bound copper(II) complexes of pyridine or 4-(N,N-dimethylamino)-pyridine (DMAP) on non-porous silica spheres, as catalysts for continuous oxidation of 2,6-disubstituted phenols, has been accomplished [28-30]. Unfortunately, very low catalytic activity and specificity of pyridine-based catalysts [31] and instability of DMAP-based catalysts in a continuous process [30] prevent their application.

In this dissertation, studies on immobilization of polymer-bound imidazole copper(II) complexes on non-porous silica particles as catalysts for the oxidative coupling polymerization of DMP are presented. This investigation was aimed at:

a) Synthesis and optimization of immobilized polymeric imidazole copper(II) complexes with high catalytic activity and specificity as well as good stability.
b) To reveal the relations between the structure of complexes as catalytic precursors and their catalytic activity or specificity; and possible reasons of reduced activity of polymeric catalysts after their immobilization.
c) To present a preliminary application of the imidazole copper(II) catalysts in the preparation of PPO-type telechelics in a batch-type reactor. (PPO or PPE stands for poly(2,6-dimethyl-1,4-phenylene oxide)).
d) To contribute to a further understanding of the mechanism of oxidative coupling from studies of the imidazole copper(II) catalytic systems.

In this introduction, a short survey on immobilization of polymer-bound catalysts and on oxidative coupling polymerization of DMP is presented. In addition, a choice of the catalytic system is discussed, then followed by an outline of this thesis.

1.1 Immobilization of Polymeric Catalysts

In general, immobilization of linear soluble macromolecular chains containing catalytic sites can be achieved mainly through four different methods as shown in Fig.1. The first class is that of highly crosslinked polymers, designated as macroporous or macroreticular resin (Fig.1, type a). This type of spherical resin can be prepared via suspension polymerization, for example, of styrene with 10-60% mol. divinylbenzene in mixed solvent/non-solvent media [32]. Swellable, lightly crosslinked, gel-type resins constitute the second group (Fig.1, type b). Examples of these

microporous beads include polystyrene crosslinked with ~2% mol. divinylbenzene [1]. Another novel way to immobilize polymeric catalysts is that of the complexation of polycations containing catalytic sites with polyanions or vice versa (Fig.1, type c). The obtained polyelectrolyte complexes can even be incorporated in a sandwich membrane-like structure under appropriate conditions [33]. These three kinds of immobilized polymeric catalysts are belonging to the class of heterogeneous catalysts. So, more or less diffusional limitation of reactants and non-uniform distribution of catalytic sites are often the main drawbacks in these cases [34]. In addition, Schouten also developed a "single crystal" method for immobilization of polymer-bound catalysts using isotactic polystyrene single crystals as support [25].

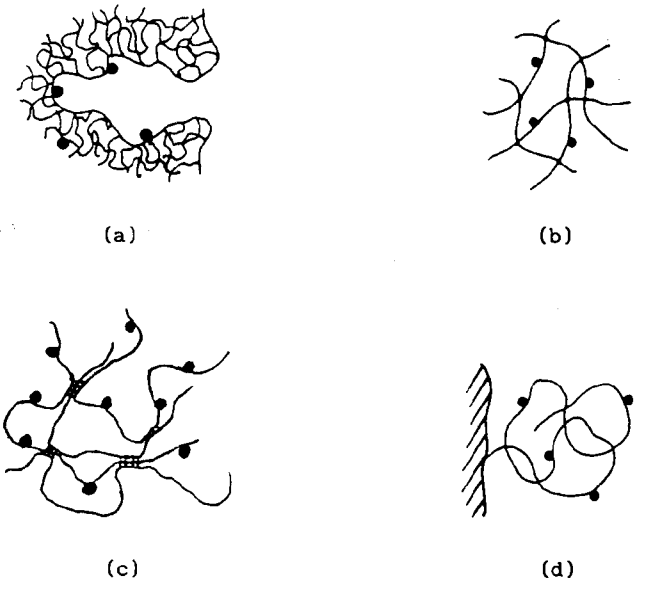


Fig.1 Schematic representation of different ways to immobilize the polymeric catalysts; (●) catalytic species. (see text)

Anchoring the linear macromolecular chains to an inert support (Fig.1, type d) seems to be a more effective approach to obtain immobilized polymeric catalysts because it may combine the advantages of both homogeneous and heterogeneous catalysts. In this case, the support itself is relatively at a larger distance from the catalytic sites when compared with the other examples

mentioned above (Fig.1, types a-c). Besides, the soluble polymer coils attached to the surface of the support might behave like separate microreactors. This situation is nearly similar to that of soluble linear macromolecules in homogeneous catalysis. Furthermore, this type of immobilization can be achieved by means of several techniques, e.g. macromolecular chain end group reaction [35], graft (co)polymerization of functional monomers [28,36], adsorption [37] or quaternization of macromolecular chains on non-modified or modified support surface, etc.. This thesis involves studies on immobilization of polymeric imidazole copper(II) catalysts on non-porous silica particles via adsorption, quaternization and graft copolymerization.

1.2 Oxidative Coupling of Phenols

Generally, oxidative coupling of phenols can give a lot of products [38,39], depending on the starting phenolic compound and the reaction conditions. However, as first described by Hay et al. in 1959 [15], copper-amine complexes can catalyze the polymerization of DMP under mild reaction conditions resulting in only two major coupling products. As illustrated in Scheme 1, apart from the main PPO production a side reaction yields the colored DPQ (3,5,3',5'-tetramethyl-4,4'-diphenoquinone). It is clear that this type of reaction can be in principle designated as "dehydrogenation of phenols". The presence of formed DPQ not only reduces the polymer PPO yield, but also strongly affects the properties of PPO as an engineering material [22]. In case of 2,6-di-tert-butylphenol (DTBP) as substrate (Scheme 1), only one coupling product, i.e. its corresponding DPQ, is obtained [40]. Because of the outstanding properties of PPO and its commercial importance [22] a large number of groups have investigated this polymerization reaction, based on different reaction systems and under different reaction conditions [15-22,40-44,46-59].

Tsuchida et al. [44] successfully applied the Michaelis-Menten kinetics to the oxidative coupling polymerization of DMP under certain reaction conditions. The Michaelis-Menten kinetics is originally derived from enzyme catalysis and indicates an equilibrium complexation between catalyst and substrate before the rate-determining step [45]. However, this polymerization reaction appears to be very sensitive to the reaction systems. So, some other type of kinetics was also proposed by Price [46].

A radical mechanism of the oxidative coupling polymerization of DMP has been proposed [20,44,46-51], including the dissociation-redistribution process

and the rearrangement mechanism [52,53]. However, Kresta suggested a cationic mechanism of the C-O coupling resulting in PPO formation [54-56]. On the contrary, a cationic mechanism was also reported by Waters [57] and Revillon [58,59] for the C-C coupling yielding DPQ. In fact, aryloxenium ions have been invoked as intermediates in phenol oxidations and in biomimetic oxidative coupling reactions [57,60]. Furthermore, many methods are also developed for generation of the aryloxenium ions [61,62]. Challa and co-workers applied the cationic mechanism to describe the catalysis of copper(II) complexes of N,N,N',N'-tetramethyl-1,2-ethanediamine (tmed) [63] and DMAP [64] for the oxidative coupling polymerization of DMP. In these cases, two one-electron transfers to coordinated molecular oxygen from one phenolate anion via copper ions take place, yielding a phenoxonium cation. Then, the formation of PPO dimer or DPQ can be accomplished through C-O or C-C coupling of the reactive phenoxonium cation with DMP.

1.3 Choice of the Catalytic System

In this thesis, N-substituted imidazole-based ligands are used in copper(II) complexes as catalysts for the oxidative coupling polymerization of DMP. This choice was based on the following considerations:

a) N-substituted imidazole-based copper(II) complexes possess higher intrinsic activity than complexes with pyridine [65,66]. On the other hand, instability of the very active DMAP-based catalysts in a continuous catalytic process results from too strong a basicity of the DMAP ligands [30]. As N-substituted imidazole ligands are of mild basicity [67] compared with DMAP, immobilized polymeric imidazole-based copper(II) complexes were expected to be promising catalysts for continuous oxidation of phenols.

b) In case of Cu(II)-tmed complexes as catalysts for the oxidative coupling polymerization of DMP, about 115% dioxygen uptake (calculated from total DMP conversion) might indicate that tmed ligands can be co-oxidized during this oxidation reaction [23]. However, when using N-substituted imidazole-based ligands in copper(II) complexes, control experiments showed that up to 97% dioxygen consumption was observed. This seems to exclude the co-oxidation of N-substituted imidazole ligands. In addition, many primary and secondary amines can react with the formed PPO polymer, e.g. an amine ligand is often incorporated into a PPO molecule on the head position [68]. This is unfavorable for the properties of PPO as an engineering plastics. However, N-substituted imidazoles are tertiary amines and are not readily incorporated into the PPO polymer [68].

c) N-vinylimidazole is a polymerable monomer containing a coordinating group and is commercially available. It can be easily copolymerized with other monomers, like styrene. This features supply a simple way to obtain the imidazole-based polymeric catalysts with different ligand contents and facilitate the immobilization of catalysts via graft copolymerization.

On the other hand, the oxidative coupling polymerization of DMP is chosen as a modal reaction for the applied catalytic system because this oxidation reaction yields only two major products, i.e. PPO and DPQ and often exhibits simple Michaelis-Menten kinetics. This has enabled us to readily determine the catalytic activity and specificity of catalysts by measuring the dioxygen consumption versus reaction time and the formed DPQ concentration, respectively. When using DTBP as a substrate in a continuous oxidation process, the stability of catalysts can be easily determined by means of continuous UV/VIS spectroscopic measurement of the sole product DPQ. Finally, continuous production of PPO oligomers or PPO-type telechelics by applying immobilized polymeric catalysts may be interesting for preparing starting materials for new block copolymers.

1.4 Outline of this Thesis

In **this chapter**, a general introduction to the immobilization of polymer-bound catalysts and the oxidative coupling (polymerization) of phenols is given with the aims of placing this investigation in a certain perspective and the explanations of the choice of a suitable catalytic system.

Chapter 2 describes the catalytic properties of low molar mass copper(II) complexes of N-methylimidazole (Cu(II)-NMIm) in the oxidative coupling polymerization of DMP. The correlation between the structures of complexes as catalytic precursors and their catalytic activity or specificity is elucidated from EPR spectroscopic analyses of complex solutions. The importance of hydroxide as co-catalyst is stressed. A suitable solvent system for better specificity of catalysts could be selected

A similar study on copper(II) complexes of poly(styrene-co-N-vinylimidazole) (Cu(II)-PS-Im) is presented in **chapter 3**. Attention is focused on some polymer effects on the catalytic activity, such as polymer chain loading with imidazole group, overlapping polymer coils, steric hindrance of polymer backbone, copper concentration in separate polymer coils, etc.. Additional information is obtained from a comparison of the catalytic properties with that of the low molar mass Cu(II)-NMIm catalyst in different solvent systems.

Chapter 4 deals with the immobilization of Cu(II)-PS-Im on silica by adsorption or quaternization process. Optimization of the reaction conditions for these immobilized catalysts in a batch-type reactor is established. Furthermore, their stability in a continuous oxidation process is tested.

Preparation of immobilized Cu(II)-PS-Im by graft copolymerization and optimization of its catalytic properties, including the stability in a continuous process, are the subjects of **chapter 5**. A comparison of the several N-substituted imidazole-based catalytic systems described in chapter 2-5 is presented. An explanation for the reduced activity of immobilized catalysts, compared with the free Cu(II)-PS-Im, is derived from some theoretical estimations and EPR spectroscopic observations.

Chapter 6 presents the preliminary application of the Cu(II)-NMIm catalytic system for the preparation of difunctional PPO-type telechelics, including ^{1}H-NMR and GPC studies of the obtained telechelics and a brief discussion of the reaction mechanism.

Finally, **chapter 7** summarizes most experimental results of chapter 2-6 and describes a possible mechanism, via a phenoxonium intermediate, of oxidative coupling polymerization of DMP catalyzed by imidazole-based copper(II) complexes.

Parts of this thesis have been published (chapter 2, 3, 4, and 7) [69-72], have been accepted for publication (chapter 5 and 6) [73,74] or are submitted for publication (chapter 7) [75].

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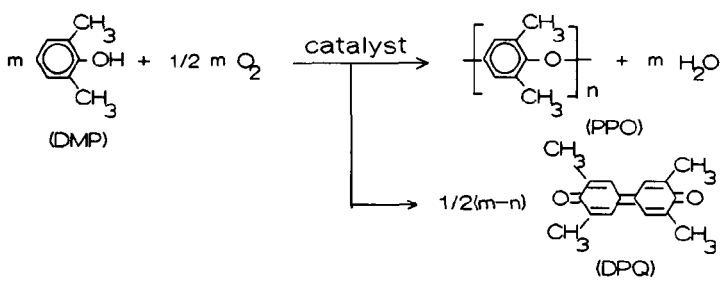
Chapter 2

Oxidative Coupling Polymerization of 2,6-Dimethylphenol Catalyzed by Copper(II) Complexes of N-methylimidazole

Abstract: The oxidative coupling polymerization of 2,6-dimethylphenol (DMP) catalyzed by copper(II) complexes of N-methylimidazole (Cu(II)-NMIm) in toluene/iso-propanol (13/2 v/v) or 1,2-dichloro-benzene/methanol (ODCB/MeOH) (13/2 v/v) was investigated. EPR spectra of these complexes indicated that the complex had a mononuclear structure in solution for higher ligand/copper ratios. The mononuclear complex was found to be a better catalyst precursor for the reaction and more favorable for poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) formation than dinuclear complexes. A main role of hydroxide appears to be to give the reactive phenolate anions from DMP. In toluene/iso-propanol, Michaelis-Menten kinetics was observed for the reaction under standard conditions with k_2=0.15 s^{-1} and K_m^{-1}=9.1 $dm^3.mol^{-1}$. Also, a better catalytic specificity for PPO formation and a higher molar mass of PPO ($\bar{M}_n$=78,300) were obtained in toluene/iso-propanol than in ODCB/MeOH. At reaction temperatures of 5-25^{0}C in toluene/iso-propanol, a yield of only 0.8-1% of the side product DPQ was achieved by adding the DMP solution slowly to the reacting system.

2.1 Introduction

The oxidative coupling polymerization of DMP, catalyzed by homogeneous copper-amine complexes yielding C-O and/or C-C coupled products [1] (Scheme 1), is not only an important industrial process, but it is also of scientific



Scheme 1

interest. Generally, copper(II) complexes of N,N,N',N'-tetramethylethylene-diamine (tmed) or pyridine as well as their derivatives have been used as effective homogeneous catalysts for this reaction [1-3]. In view of industrial applications, it seems useful to attach homogeneous catalysts to an inert support, like silica, in order to facilitate separation of catalysts from products and to make their re-use possible. In this laboratory, we started an investigation on immobilization of copper(II) complexes of polymer-bound imidazole as catalysts for the oxidative coupling polymerization of DMP [4,5]. However, so far no detailed and systematic study on their low molar mass imidazole analogues, like Cu(II)-NMIm complexes, was described. Therefore, in the present paper dealing with Cu(II)-NMIm as catalyst, the relations between the structure of the complexes as catalyst precursor and their activity as well as specificity are revealed. The reaction kinetics and general reaction process will also be discussed. Particularly, we shall focus attention on the effects of solvent systems on the catalytic specificity as well as the molar mass of PPO obtained from this polymerization. It appears that this study gives an useful background for our research on the immobilized polymer-bound catalysts.

2.2 Experimental

2.2.1 Materials

$CuCl_2(H_2O)_2$ was obtained analytically pure from Merck. NMIm (Aldrich) was distilled from KOH under reduced N_2 pressure. DMP (Aldrich) was purified by repeated recrystallization from n-hexane. NaOH, LiOH, KOH, iso-propanol and methanol (Uvasol quality) (Merck) were used without further purification. Toluene (dried over Na) and ODCB (distilled under reduced N_2 pressure from CaH_2) were also from Merck.

2.2.2 Spectroscopic analysis

The EPR spectra of frozen solutions of Cu(II)-NMIm complexes were recorded on a Variam E-3 (X-band) Spectrometer at -196°C. The same standard conditions as for oxidative coupling polymerization were applied except that no DMP was added to the system.

2.2.3 Oxidative coupling polymerization

The standard reaction conditions for oxidative coupling were: T= 25°C; Po_2= 101.3 kPa; [DMP]= 0.06 mol.dm^{-3}; [Cu^{2+}]= [OH^-]= 0.033x[NMIm]= 3.32

$mmol.dm^{-3}$; solvent mixture, toluene/iso-propanol (13/2 v/v) or ODCB/MeOH (13/2 v/v); total reaction volume, 0.015 dm^3. Hydroxide was added as NaOH in iso-propanol or as LiOH or KOH in methanol. Steady state reaction rates R were found by measuring O_2 uptake as a function of time with an automatic isobaric gas burette. The shaking speed of the reaction vessel was sufficient to prevent gas-liquid diffusion of O_2 from becoming rate determining. For experiments in which DMP was slowly added at a constant rate to a reacting system, a perfusor syringe injector was used. These reactions were carried out in a three-necked flask, equipped with a septum stopper and a magnetic stirring bar, under O_2 atmosphere.

2.2.4 Determination overall catalytic specificity

Once the reaction was complete the reaction mixture was immediately diluted with chloroform (for the toluene/iso-propanol system) or ODCB/MeOH (for the ODCB/MeOH system) and subsequently the concentration of DPQ was determined with a PYE Unicam SP-8-200 UV/VIS Spectrophotometer at 421 nm (ε=74,000 $dm^3.mol^{-1}.cm^{-1}$) or 426 nm (ε=61,000 $dm^3.mol^{-1}.cm^{-1}$). From these data, the percentage of reacted DMP that had been transformed into DPQ was calculated because PPO and DPQ are practically the sole products.

2.2.5 Determination of $\bar{M}_n$, T_g and T_d

After O_2 consumption had ceased, the polymer was precipitated in methanol containing 5 wt% HCl. The polymer was further purified three times by precipitation from a chloroform solution in methanol with 5 wt% HCl. The resulting white polymer was dried under vacuum for at least 24 hours. $\bar{M}_n$ of PPO was determined with a Knauer Membrane Osmometer in chloroform. The glass-transition temperature T_g and decomposition temperature T_d of PPO were measured under N_2 atmosphere with a Perkin-Elmer DSC-2 and a Perkin-Elmer DSC-1B, respectively.

2.3 Results and Discussion

2.3.1 The structure of Cu(II)-NMIm in solution

The VIS spectra of the Cu(II)-NMIm complexes in toluene/iso-propanol (13/2 v/v) for ligand/copper ratios varying from 0 to 30, originating from the d-d absorption, show that the absorption maximum of the complex shifts from 800 nm to 630 nm with increasing ligand/copper ratio. Another UV absorption band around 300 nm could be an indication of Cu-Cu interaction as found in

dinuclear copper complexes [6]. Unfortunately, the strong effect of the charge-transfer absorption in this area prevents observation of the dimer copper complex.

Thus UV/VIS spectroscopy is insufficient and EPR spectra are needed to indicate the structure of the complex. Generally, mononuclear copper(II) complexes exhibit an EPR signal because of the presence of an unpaired electron in a Cu^{2+} d-orbital. In addition, the interaction of the unpaired electron with the magnetic moments of the copper nucleus and the nuclei of the ligands may result in a superhyperfine structure. However, dinuclear copper(II) complexes are often EPR-silent because of a large singlet-triplet splitting, resulting from the effective anti-ferromagnetic coupling, with a small population of the upper (EPR active) level [7].

The EPR spectrum of a frozen solution of $CuCl_2$ in toluene/iso-propanol (13/2 v/v) shows the presence of $CuCl_2$(iso-propanol)$_x$ species (Fig.1 (a): $g_\perp$=2.08, $g_{//}$=2.37, $A_{//}$=130 Gauss). The addition of ligand leads to complete disappearance of the EPR signal of $CuCl_2$(iso-propanol)$_x$. Obviously, $CuCl_2$(iso-propanol)$_x$ is converted into other species, one of them being the typical EPR-detectable mononuclear $Cu(NMIm)_4^{2+}$ complex with the very clear superhyperfine splitting [8] (Fig.1 (b)-(d): $g_\perp$=2.06, $g_{//}$=2.29, $A_{//}$=180 Gauss). Although the EPR spectra were not integrated, it is clear from Fig.1 that, especially for Cu(II)$(NMIm)_n$(OH)Cl, variation of the ligand/copper ratio from n=1 to 30 gives a gradual enhancement of the EPR signal of the $Cu(NMIm)_4^{2+}$ species (Fig.1 (b)-(d); note the decreasing receiver gain values). Furthermore, we found a first-order dependence of the reaction rate on total catalyst concentration $[CuCl_2]_0$ at n=30, which indicates that, in this case, almost all complexes in the solution are mononuclear. On the other hand, weaker EPR-signals of $Cu(NMIm)_4^{2+}$ at lower ligand/copper ratios imply that some other, EPR-silent, species must be present in the solution, probably a dinuclear complex. Finally, it is notable that some peak-shoulders in the EPR spectra of $Cu(NMIm)_4^{2+}$ are observed for low ligand/copper ratios and disappear for ligand/copper>3 (Fig.1 (b)-(c)). This probably indicates that monomeric $Cu(NMIm)_y$(iso-propanol)$_{6-y}^{2+}$ (y=2-4) species are also present in the solution.

So, from the EPR spectra it is deduced that increase of the ligand/copper ratio for Cu(II)-NMIm causes transformation of a dinuclear complex and a few $Cu(NMIm)_y$(iso-propanol)$_{6-y}^{2+}$ species into mononuclear $Cu(NMIm)_4^{2+}$ complex. This transformation is almost complete at ligand/copper=30 as indicated in Scheme 2.

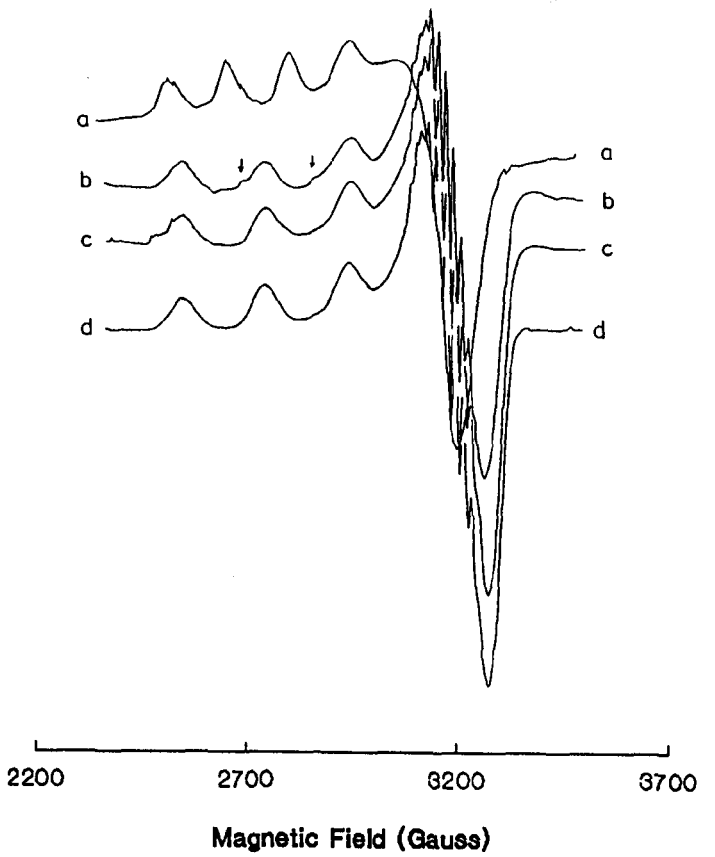
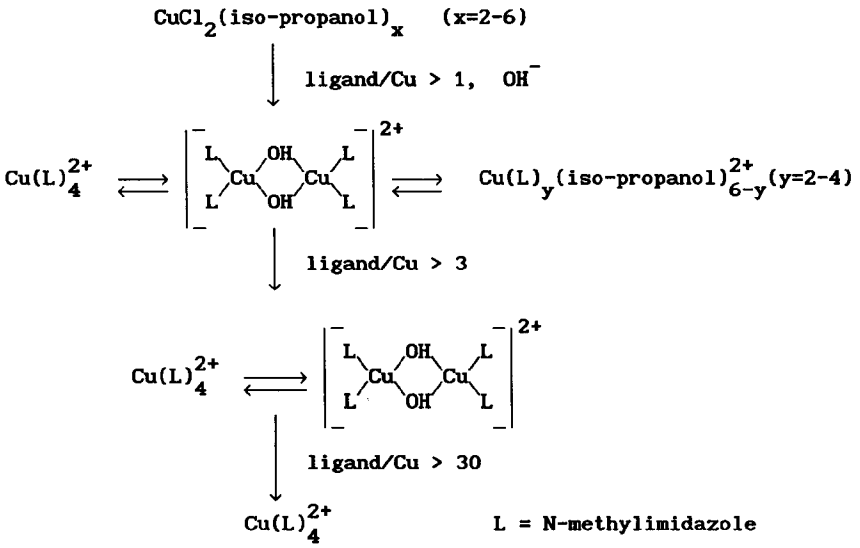


Fig.1 EPR spectra of Cu(II)-NMIm complexes in toluene/iso-propanol (13/2 v/v) ($[CuCl_2]$=3.32 mmol.dm^{-3}).
(a) ligand/Cu=0, OH/Cu=0, receiver gain (RG)=2x10^4;
(b) ligand/Cu=1, OH/Cu=1, RG=8x10^4;
(c) ligand/Cu=3, OH/Cu=1, RG=3.2x10^4;
(d) ligand/Cu=30, OH/Cu=1, RG=1.25x10^4.

2.3.2 The role of hydroxide

The reaction rates under standard conditions in toluene/iso-propanol are plotted as a function of the OH/Cu ratio in Fig.2. No difference is found by using either LiOH (KOH) or NaOH, but the reaction does not proceed in the absence of base. Furthermore, when the base is added to the DMP solution instead of to the Cu(II)-NMIm solution, much higher reaction rates and shorter

induction period (Δt) are observed, especially for higher OH/Cu ratios. These



Scheme 2

effects seem to suggest that dehydronation of DMP by hydroxide ion as shown in the next equation is essential for coordination of substrate to the Cu(II)-NMIm complex:

$$[OH^-] + [PhOH] \rightleftarrows [PhO^-] + [H_2O]$$

In both cases a maximum in the reaction rate is observed at OH/Cu=1.0 and 1.4, respectively (Fig.2). This result indicates that increasing hydroxide concentration promotes formation of phenolate anions, resulting in increasing reaction rates, but an excess of hydroxide somehow destroys the catalyst, causing a decrease of reaction rates. Addition of hydroxide to the substrate solution shortens the contact time of copper complex with base and prevents more catalysts from being destroyed for higher OH/Cu ratios. So, in this case higher reaction rates and a shift of the optimum catalytic activity are observed. This explanation is supported by EPR studies. In EPR experiments the signals of Cu(II)-NMIm in toluene/iso-propanol at ligand/copper=30 have about the same intensity for OH/Cu=0.5 and 1.0, but decline markedly for OH/Cu=1.5. Therefore, in agreement with suggestions by others [9-11], we believe that also in the present case hydroxide plays primarily a role as so-called co-catalyst for the formation of phenolate anions.

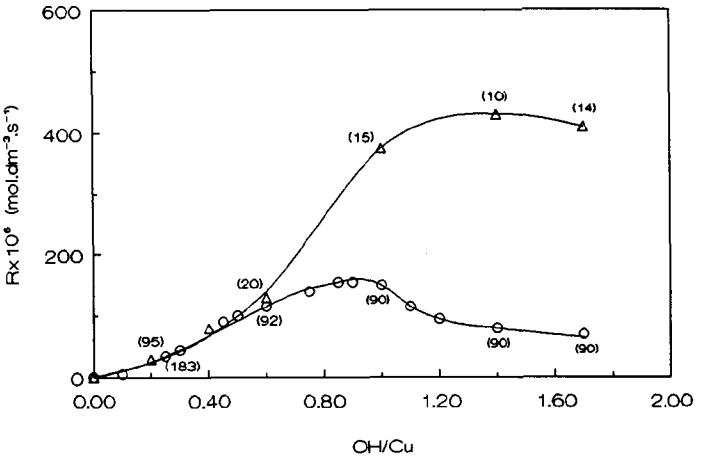


Fig.2 Steady state reaction rate as a function of OH/Cu ratio under standard conditions in toluene/iso-propanol.
(o) adding base to Cu(II)-NMIm catalytic system;
(Δ) adding base to DMP solution.
In parenthesis the induction period (Δt)=(X) sec is given.

2.3.3 Effect of ligand/copper ratio

As shown in Fig.3 for Cu(II)-NMIm in toluene/iso-propanol, the reaction rates under standard conditions increase with increasing ligand/copper ratio. Below ligand/copper=5, a small amount of a yellow precipitate was observed in the catalyst solution before the oxidative coupling experiment started. In accordance with the EPR spectroscopic results, it is clear that a higher ligand concentration not only enhances the stability of Cu(II)-nmim species against base in the catalyst solution but also promotes formation of mononuclear complex, which seems to be a good catalyst precursor in the oxidative coupling polymerization of DMP. Moreover, the basicity of the reaction mixture is enhanced in case of very high ligand concentration (up to ligand/copper=40), thus promoting the dehydronation of DMP and resulting in increasing reaction rates. Therefore, the consumption rates of O_2 continue to increase even above ligand/copper=30. The same catalytic as well as spectroscopic results under standard conditions are observed in ODCB/MeOH although no precipitation is found for low ligand/copper ratios. In ODCB/MeOH (13/2 v/v) the same reaction was also investigated by Verlaan [12] and

Meinders [13] only for low ligand/copper ratios. Therefore, a three-fold higher reaction rate is observed in the present case for ligand/copper=30 than in Verlaan's case for ligand/copper=6. This indicates again that a very high ligand/copper ratio yielding a mononuclear complex is necessary for obtaining a high catalytic activity. In Meinders' case, still lower reaction rates were found because of the use of air instead of pure O_2.

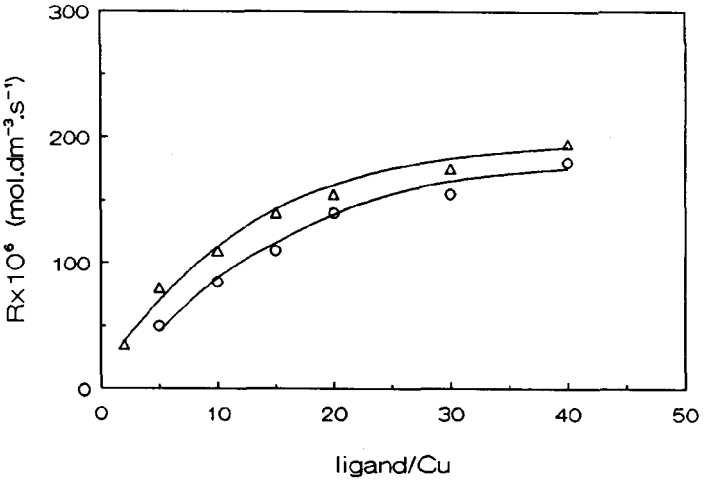


Fig.3 Steady state reaction rate as a function of ligand/Cu ratio under standard conditions. (o) in toluene/iso-propanol; (Δ) in ODCB/MeOH.

2.3.4 Effect of copper counterions

For the mononuclear copper(II) complexes of 4-dimethylaminopyridine (Cu(II)-DMAP), it was found that coordinating Cl^- counterions are also proper bridging ions for the dimerization of copper complexes, necessary for the re-oxidation of Cu(I) to Cu(II) [3,14]. However, in the present case with standard conditions in ODCB/MeOH, the same reaction rates are observed when using either $CuCl_2$ or $Cu(ClO_4)_2$ (ODCB/MeOH was used as solvent because $Cu(ClO_4)_2$-NMIm complexes precipitate in toluene/iso-propanol). This result means that the phenolate anion, instead of the non-coordinating ClO_4^-, can probably also act as bridging ion in the dimerization.

2.3.5 Kinetics of oxidative coupling

The reaction rates under standard conditions become independent of Po_2 for Po_2>100 kPa indicating that oxidation of substrate (k_2) was measured rather than re-oxidation of Cu(I).

Under standard conditions in toluene/iso-propanol, the reaction rates were measured for different DMP concentration. So-called saturation kinetics, as found in reactions catalyzed by enzymes [15], are observed, and the double-reciprocal Lineweaver-Burk plot of reaction rate versus DMP concentration is given in Fig.4. A straight line intersects the Y-axis in agreement with the well-known equation:

$$\frac{1}{R} = \frac{1}{k_2[E]_0} + \frac{K_m}{k_2[E]_0[DMP]}$$

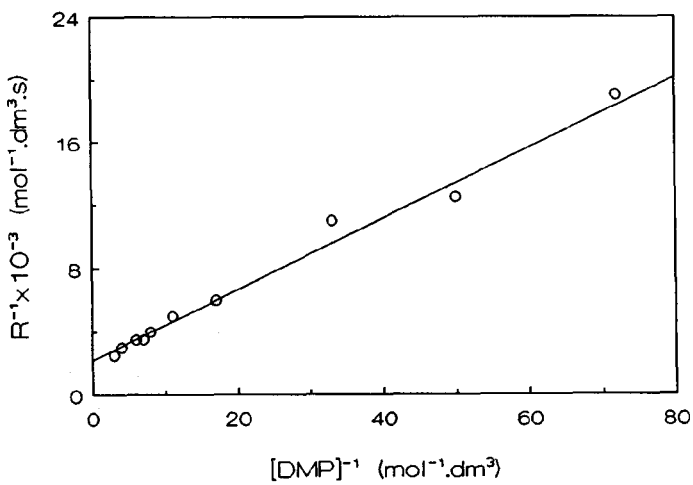
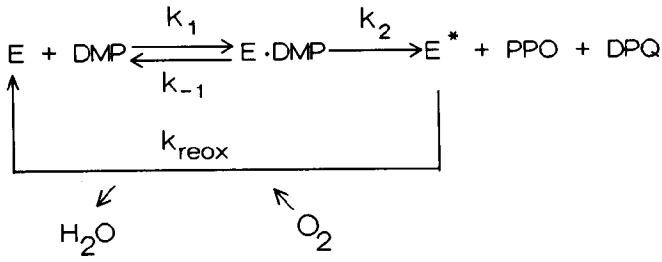


Fig.4 Lineweaver-Burk plot of steady state reaction rate versus substrate concentration under standard conditions in toluene/iso-propanol.

Particularly, saturation kinetics in DMP concentration was also found when adding the base to the substrate solution although all reaction rates were higher (see Fig.2). This means that the phenolate anion-containing copper complex should react with a DMP molecule before the rate-determining step takes place. Therefore, the oxidative coupling polymerization of DMP catalyzed by Cu(II)-NMIm in toluene/iso-propanol can be described by a Michaelis-Menten mechanism as shown in Scheme 3. Here, E is the Cu(II)-NMIm-phenolate anion

complex; E^* is the Cu(I) complex; $[E]_0$= overall concentration of copper salt; k_2= rate constant of the rate-determining step and $K_m=(k_{-1}+k_2)/k_1$ (the Michaelis-Menten constant). From the straight line in Fig.4 k_2 and K_m^{-1} have been calculated yielding: $k_2=0.15\ s^{-1}$ and $K_m^{-1}=9.1\ dm^3.mol^{-1}$ (a measure for the accessibility of the catalytically active site for the substrate). These values show that the NMIm-based copper(II) complex is a good catalyst precursor for the oxidative coupling polymerization of DMP under the applied experimental conditions.



Scheme 3

2.3.6 Specificity

The specificity of the oxidative coupling polymerization of DMP catalyzed by Cu(II)-NMIm complexes was studied under standard conditions in toluene/iso-propanol and in ODCB/MeOH. In Fig.5 both solvent systems show enhanced PPO formation with increasing ligand/copper ratios, but for ligand/copper ratio>30, no further improvement of specificity is observed. Considering the EPR spectroscopic results, this indicates that the mononuclear Cu(II)-NMIm complex as catalyst precursor is favorable for C-O coupling leading to PPO formation. It should be also noted that in all cases the specificity in toluene/iso-propanol is better than in ODCB/MeOH (Fig.5). Such a result was also reported by Viersen et al. [16] using the Cu(II)-tmed complex as catalyst for the same polymerization reaction.

From Fig.6 it is obvious that the major fraction of DPQ is formed early in the reaction period. For these experiments under standard conditions in toluene/iso-propanol, the reaction were stopped by adding excess of $LiClO_4$ in order to precipitate the copper complexes and the concentration of DPQ was determined at once. Consequently, the specificity for PPO should further improve when adding slowly the DMP solution to the reacting system. Indeed, in

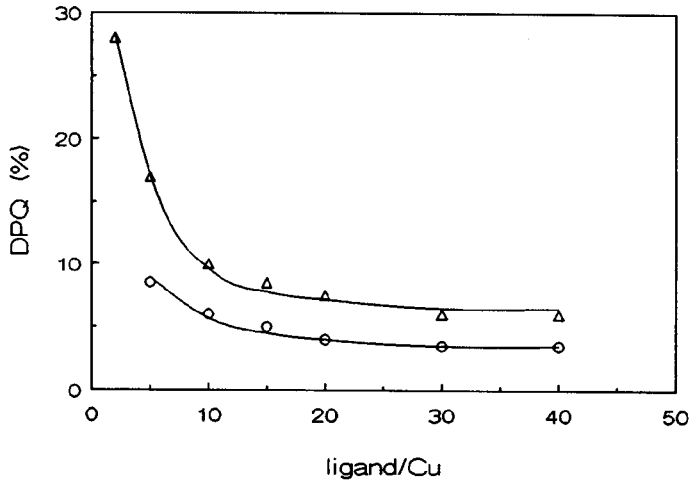


Fig.5 Effect of ligand/Cu ratio on specificity under standard condition.
(o) in toluene/iso-propanol; (Δ) in ODCB/MeOH.

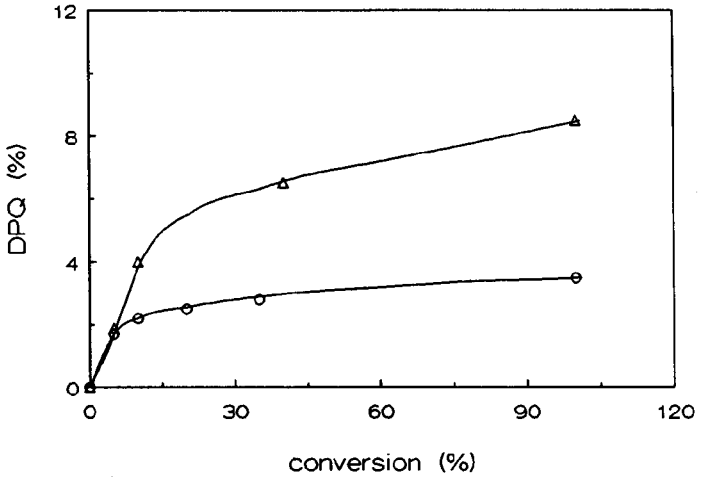


Fig.6 The formation of DPQ as a function of the conversion under standard conditions in toluene/ iso-propanol.
(o) ligand/Cu=30; (Δ) ligand/Cu=5.

Fig.7 for toluene/iso-propanol with standard conditions, the yield of DPQ is even reduced to 1% when adding the substrate to the reacting system with a rate of 0.16 ml.min^{-1}. In addition, the results in Fig.7 show also that lowering of the reaction temperature can further promote PPO formation as found for other catalytic systems [17].

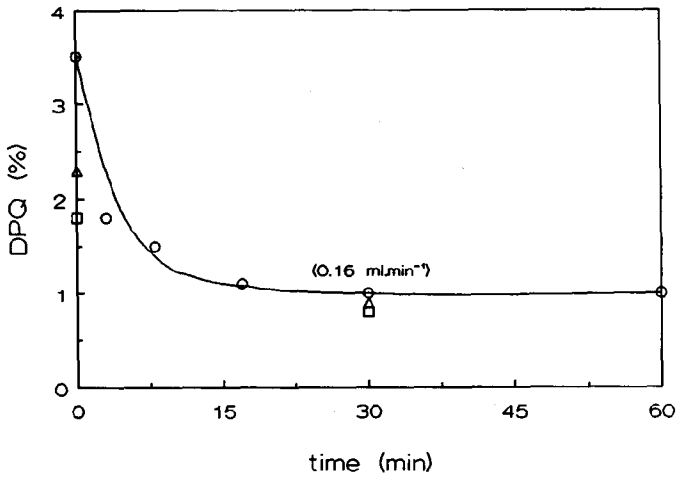


Fig.7 Effect of the rate of adding 5 ml (0.18 mol.dm^{-3}) DMP solution to Cu(II)-NMIm catalytic system on specificity under standard conditions in toluene/ iso-propanol.
(o) T=25°C; (Δ) T=15°C; (□) T=5°C.

2.3.7 $\bar{M}_n$, T_g and T_d of PPO

The molar mass ($\bar{M}_n$), glass-transition temperature (T_g) and degradation temperature (T_d) of PPOs obtained from both solvent systems are summarized in Table 1. It is very significant that the molar mass of PPO synthesized in toluene/iso-propanol is much higher than that in ODCB/MeOH. Accordingly, a 5°C higher value of T_g and 18°C higher value of T_d are observed for PPO from toluene/iso-propanol. It should be remembered that also a better reaction specificity for PPO formation is obtained in toluene/iso-propanol. Toluene/iso-propanol (13/2 v/v) therefore appears to be a suitable solvent mixture for the oxidative coupling polymerization of DMP catalyzed by Cu(II)-NMIm complexes.

Table 1. Characteristics of PPO obtained from oxidative coupling polymerization of DMP catalyzed by Cu(II)-NMIm complexes in different solvent systems under standard conditions except: [DMP]=0.18 mol.dm^{-3}, and LiOH/Cu=1.6 in ODCB/MeOH (13/2 v/v)

	$\bar{M}_n$	$[\eta]$(dl/g)*	T_g(^oC)	T_d(^oC)
in toluene/iso-propanol	78,300	0.96	215	241
in ODCB/MeOH	30,900	0.42	210	223

* intrinsic viscosity (solution of PPO in $CHCl_3$ at 30^oC)

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Chapter 3

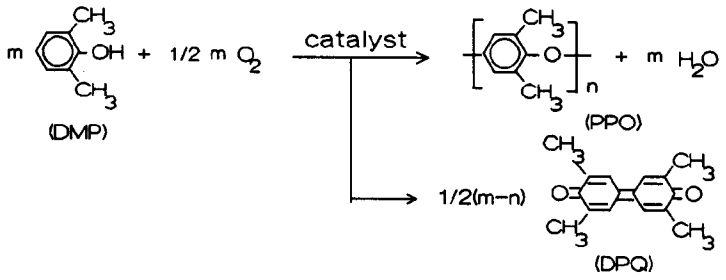
Oxidative Coupling Polymerization of 2,6-Dimethylphenol Catalyzed by Copper(II) Complexes of Poly(styrene-co-N-vinylimidazole)

Abstract: The oxidative coupling polymerization of 2,6-dimethylphenol (DMP) catalyzed by copper(II) complexes of poly(styrene-co-N-vinylimidazole) (Cu(II)-PS-Im) in toluene/iso-propanol (13/2 v/v) was investigated. The EPR spectra of these complexes indicate that the complex had a mononuclear structure $Cu(PS\text{-}Im)_4^{2+}$ in solution for higher ligand/copper ratios. This mononuclear complex was found to be a better catalyst precursor for the reaction and more favourable for poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) formation than dinuclear complexes. Viscometric experiments on solutions of polymeric ligands with and without copper(II) ions showed that the decreasing reaction rate for higher ligand/copper ratios may be due to too high concentrations of polymeric ligand, resulting in overlap of polymer coils. The effect of chain loading α with imidazole ligands on the catalytic activity showed an optimum value for α=0.11, which was explained predominantly in terms of strain in polymer chain segments between neighbouring ligand groups in the same copper complex. Michaelis-Menten kinetics was observed for the reaction under standard conditions with k_2=0.15 s^{-1} and K_m^{-1}=0.45 $dm^3.mol^{-1}$. The smaller K_m^{-1} for Cu(II)-PS-Im than for low molar mass copper(II) complexes of N-methylimidazole (Cu(II)-NMIm) probably originates from steric hindrance of polymer backbone and difficult substitution of polydentate ligands by substrate. The transition of reaction rates to second order in initial copper concentration indicates that dimerization of copper complexes is necessary for re-oxidation of Cu(I) to Cu(II). Methanol as cosolvent appears to be more favourable for a higher K_m^{-1} value than iso-propanol in case of Cu(II)-PS-Im as well as Cu(II)-NMIm.

3.1 Introduction

The oxidative coupling polymerization of DMP (Scheme 1) catalyzed by copper(II) complexes of immobilized polymer-bound pyridine or 4-dimethylaminopyridine (DMAP) has been extensively studied in this laboratory [1-3]. In view of the lower intrinsic activity and specificity of the pyridine-based catalysts [4] and too strong a basicity of the DMAP ligands [3], these catalysts were not suitable for continuous processes. On the other hand, copper(II) complexes of N-substituted imidazole ligands with mild

basicity [5] possess higher intrinsic activity than complexes with pyridine [6,7]. Therefore, immobilized polymer-bound imidazole copper(II) complexes were expected to be more promising catalysts for the applied reaction.



Scheme 1

Recently, we investigated Cu(II)-NMIm as catalyst for the oxidative coupling polymerization of DMP in toluene/iso-propanol (13/2 v/v) and in 1,2-dichlorobenzene/methanol (ODCB/MeOH) (13/2 v/v) [8]. It was found that mononuclear complexes as catalyst precursor are favourable for higher activity and better specificity for PPO formation than dinuclear species. Besides, better specificity for PPO formation and much higher molar mass of PPO were obtained in toluene/iso-propanol than in ODCB/MeOH.

In the present paper dealing with Cu(II)-PS-Im as catalysts, a detailed and systematic study is described of the same oxidative coupling polymerization in toluene/iso-propanol (13/2 v/v) and some other solvent mixtures. Differences in the catalytic nature of Cu(II)-PS-Im and Cu(II)-NMIm and the effect of different solvent systems on the reaction rate will be discussed.

3.2 Experimental

3.2.1 Materials

$CuCl_2(H_2O)_2$ was obtained analytically pure from Merck. N-vinylimidazole and styrene (Aldrich) were distilled from KOH under a reduced N_2 atmosphere. DMP (Aldrich) was purified by repeated recrystallization from n-hexane. NaOH, iso-propanol and methanol (Uvasol quality) (Merck) were used without further purification. Toluene (dried over Na) and ODCB (distilled under reduced N_2

pressure from CaH_2) were also from Merck.

3.2.2 Synthesis and characterization of PS-Im

Radical copolymerization of N-vinylimidazole with styrene was performed in toluene using AIBN as an initiator as described previously [9]. The $\bar{M}_n$ values of copolymer samples were determined with a Knauer Membrane Osmometer in chloroform. The chain loading α of copolymers with imidazole ligands was determined by elemental analysis. All results on synthesis and characterization are compiled in Table 1. In order to obtain copolymers with reliable and narrow ranges of α values, the final conversions of copolymerizations were taken below 15% instead of the conversions above 40% used before [10]. According to the Fineman and Ross method, the reactivity ratios of the monomers were calculated to be r_1=0.07 and r_2=7 for N-vinylimidazole and styrene, respectively. These values are similar to the values r_1=0.1 and r_2=10 given by Petrak [9] (r_2/r_1=100 in both cases).

Table 1. Data on synthesis and characterization of styrene-N-vinylimidazole copolymers with varying chain loading α[a]

Mole fraction of N-vinylimidazole	Conversion of copolymerization (%)	α	$\bar{M}_n$ of copolymers
0.15	13.9	0.03	44 300
0.31	14.8	0.05	31 000
0.34	15.0	0.07	43 000
0.52	12.3	0.11	46 000
0.62	13.4	0.17	-
0.66	8.78	0.21	-
0.71	9.34	0.23	34 000
0.81	12.0	0.35	-

[a] Copolymerizations were carried out under N_2 at 60°C for 5 hours; amount of AIBN based on total of monomers is 0.78 mole% ; toluene/monomers=1/1 (v/v).

3.2.3 EPR spectroscopy

The EPR spectra of frozen solutions of Cu(II)-PS-Im complexes in toluene/iso-propanol (13/2 v/v) were recorded on a Varian E-3 (X-band) Spectrometer at -196°C. The same standard conditions as for oxidative coupling polymerization were applied except that no DMP was added to the system.

3.2.4 Oxidative coupling polymerization

The standard conditions for oxidative coupling were: T= 25 ^{o}C; Po_2= 101.3 kPa; [DMP]= 0.06 mol.dm^{-3}; [Cu^{2+}]= [OH^-]= 0.25x[imidazole]= 3.32 mmol.dm^{-3}; solvent mixture, toluene/iso-propanol (13/2 v/v); total reaction volume, 0.015 dm^3. Polymeric catalysts were prepared in situ by dissolving the copolymeric ligands in toluene and adding $CuCl_2$/iso-propanol solution. Hydroxide was added as NaOH in iso-propanol. After saturating the reaction system with O_2, the reactions were started by mixing the catalyst solution with a solution of DMP in toluene. Steady state reaction rates R were calculated by measuring O_2 uptake as a function of time with an automatic isobaric gas burette. The shaking speed of the reaction vessel was high enough to prevent gas-liquid diffusion of O_2 becoming rate determining.

3.2.5 Determination of overall catalytic specificity

Once the reaction was complete, the reaction mixture was diluted with chloroform and the concentration of 3,5,3',5'-tetramethyl-4,4'-diphenoquinone (DPQ) was quickly determined with a PYE Unicam SP-8-200 UV/VIS Spectrophotometer at 421 nm (ε=74,000 dm^3.mol^{-1}.cm^{-1}). The percentage of reacted DMP that had been transformed into DPQ could be calculated because PPO and DPQ are practically the sole products.

3.3 Results and Discussion

3.3.1 Structures of Cu(II)-PS-Im in solution

UV spectra failed to give valuable information and EPR spectra seem to be more suitable to indicate the complex structures [8].

The EPR spectrum of a frozen solution of $CuCl_2$ in toluene/iso-propanol (13/2 v/v) shows the presence of $CuCl_2$(iso-propanol)$_x$ species (Fig.1 (i): $g_\perp$=2.08, $g_{//}$=2.37, $A_{//}$=130 Gauss). The addition of polymeric ligands with α=0.11 leads to complete disappearance of $CuCl_2$(iso-propanol)$_x$. Obviously, $CuCl_2$(iso-propanol)$_x$ is converted into some other species, one of them probably being the coordinatively unsaturated, EPR-detectable, mononuclear Cu(PS-Im)$_{1-3}^{2+}$ complex (Fig.1 (ii)-(iv), species a, $g_\perp$=2.03, $g_{//}$=2.24, $A_{//}$=140 gauss). On further increase of the ligand/copper ratio, the EPR signal of Cu(PS-Im)$_{1-3}^{2+}$ gradually decreases and disappears at ligand/copper=4 (Fig.1 (v)). At the same time, another, EPR-detectable, mononuclear Cu(PS-Im)$_4^{2+}$ complex is observed with very clear superhyperfine splitting [11] (Fig.1 (iii)-(vi), species b, $g_\perp$=2.03, $g_{//}$=2.24, $A_{//}$=180 Gauss and A_N=15 Gauss).

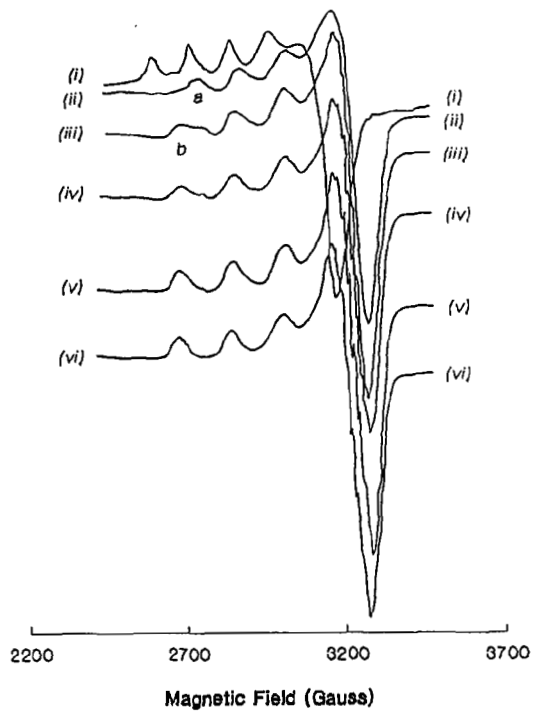
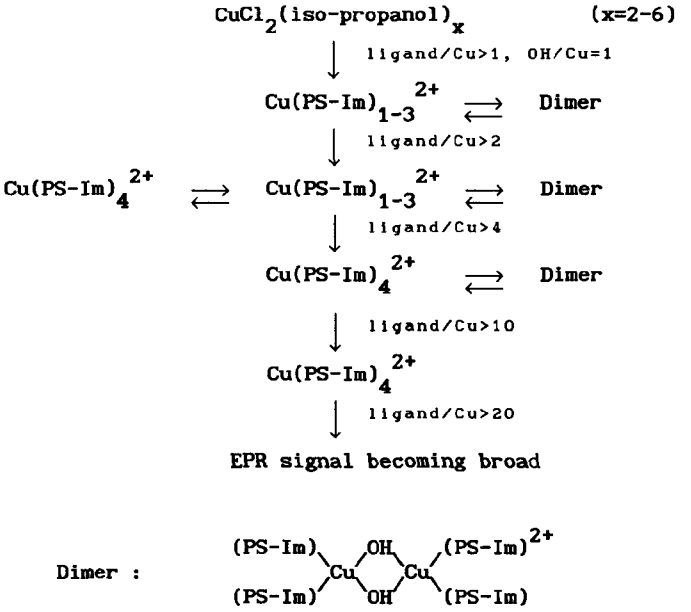


Fig.1 EPR spectra of Cu(II)-PS-Im complexes for PS-Im with α=0.11 ([Cu(II)]=3.32 mmol.dm^{-3}):
(i) ligand/Cu=0, OH/Cu=0, receiver gain (RG)=2x10^{4};
(ii) ligand/Cu=1, OH/Cu=1, RG=6.2x10^{4};
(iii) ligand/Cu=2, OH/Cu=1, RG=4x10^{4};
(iv) ligand/Cu=3, OH/Cu=1, RG=4x10^{4};
(v) ligand/Cu=4, OH/Cu=1, RG=3.2x10^{4};
(vi) ligand/Cu=10, OH/Cu=1, RG=2.5x10^{4}.

Although the EPR spectra of the complexes are not integrated, it is clear that variation of the ligand/copper ratio from 1 to 10 gives rise to a gradual enhancement of the total mononuclear complex concentration (Fig.1 (ii)-(vi); note the decreasing receiver gain values). The EPR signals of the complexes become very broad and show very low intensity for ligand/copper>20, probably due to the overlap of the polymer ligand coils in the solution (see later). On the other hand, the rather weak EPR signals of mononuclear complexes at low

ligand/copper ratios imply that some other, EPR-silent, species must also be present in the solution, probably a dinuclear complex [8,12]. Indeed, such dinuclear complexes should be gradually converted into mononuclear ones with increasing ligand/copper ratio and this transformation seems to be almost complete for ligand/copper ratio around 10 (Scheme 2 gives the overall picture).



Scheme 2

3.3.2 The role of hydroxide

The reaction rates under standard conditions are plotted as a function of the OH/Cu ratio in Fig.2. With PS-Im ligands no reaction takes place in the absence of base. When the base is added to the DMP solution instead of to the Cu(II)-PS-Im solution, much higher reaction rates and shorter induction periods (Δt) are observed. Such effects were also found for Cu(II)-NMIm system [8] and prove that dehydronation of DMP by hydroxide is essential for coordination to Cu(II)-PS-Im complexes. In both cases a maximum in reaction rate is observed, viz. at OH/Cu=2.0 and 1.5, respectively (Fig.2). This indicates that increasing the hydroxide concentration promotes formation of

phenolate anions, resulting in an enhanced reaction rate, whereas an excess of hydroxide somehow destroys the catalyst, causing a decrease in rate. Addition of hydroxide to DMP solution shortens the contact time of copper complex with base and therefore suppresses catalyst destruction, so that higher reaction rates are observed.

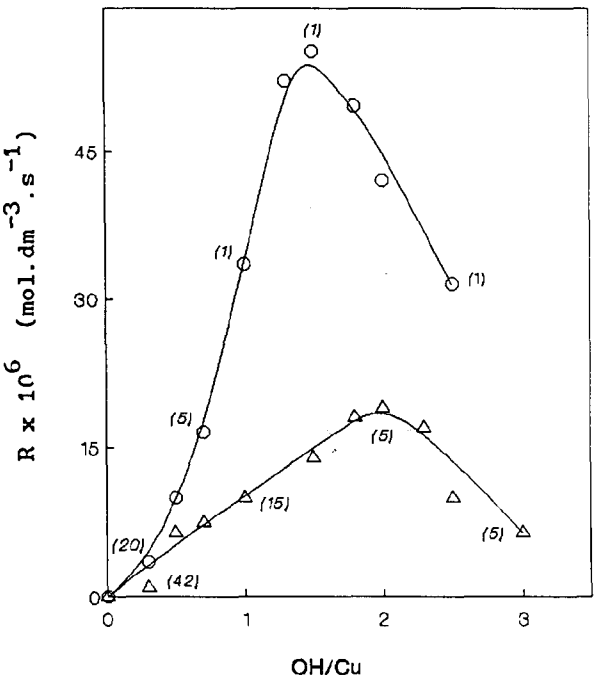


Fig.2 Steady state reaction rate as a function of OH/Cu ratio under standard conditions for PS-Im with α=0.11:
(Δ) adding base to Cu(II)-PS-Im solution;
(o) adding base to DMP solution.
The induction period Δt=(X) min is given in parentheses.

In case of adding base to Cu(II)-NMIm solution, the optimum catalytic activity was found at OH/Cu=1 [8] instead of 2 in the present case. This shift of maximum reaction rate indicates that the stability of complexes against base is improved by introduction of polymeric ligands.

3.3.3 Effect of ligand/copper ratio

As shown in Fig.3, the optimum reaction rate under standard conditions is

obtained for ligand/copper ratios around 10. In view of the spectroscopic results, it is clear that a higher ligand concentration promotes formation of mononuclear complexes, especially $Cu(PS\text{-}Im)_4^{2+}$, which seems to be a good catalyst precursor in the applied system. In the solvent mixture ODCB/MeOH (13/2 v/v) and for ligand/copper<6, Verlaan et al. [6] also found increasing reaction rates for higher ligand/copper ratios.

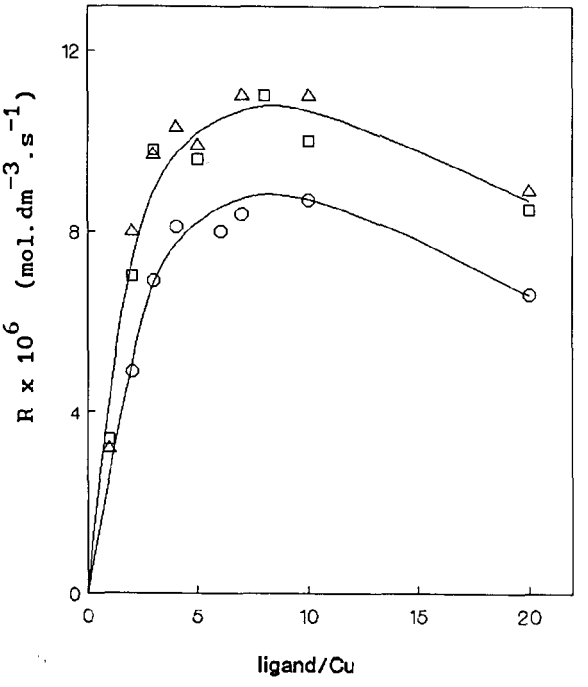


Fig.3 Steady state reaction rate as a function of ligand/Cu ratio under standard conditions for PS-Im with:
(□) α=0.07; (Δ) α=0.11; (o) α=0.23.

By performing some viscometric experiments on solutions of polymeric ligands with and without copper ions, it is observed that the specific viscosities (η_{sp}) of the solutions give a stronger increase above polymer concentrations of 0.06 $g.ml^{-1}$, which corresponds to ligand/copper=12 (Fig.4). Therefore, it is assumed that the decrease in reaction rate in Fig.3 for ligand/copper>10 is caused at least part by overlap of the polymer ligand coils. Of course, this situation is different from that for Cu(II)-NMIm, in

which case increasing reaction rates were still observed for ligand/copper> 20 [8].

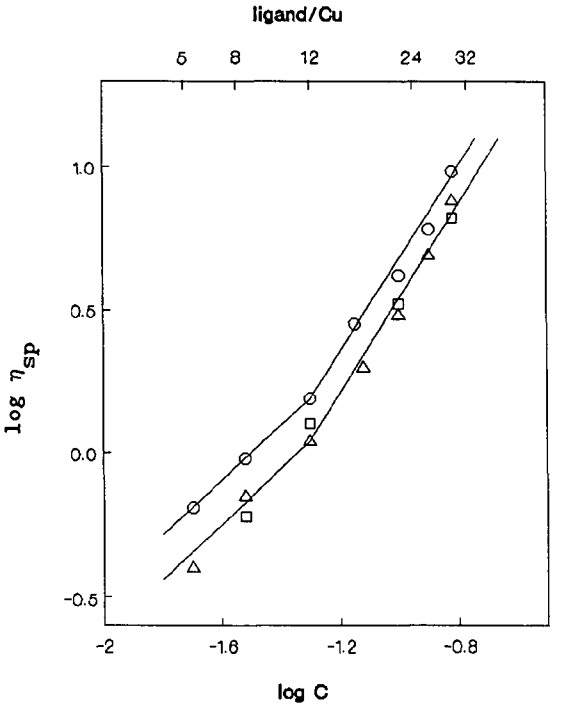


Fig.4 Plot of log (η_{sp}) versus log C (C is the concentration in g.ml^{-1}) for solutions of Cu(II)-PS-Im with α=0.07 under standard conditions:
(Δ) in toluene/iso-propanol (13/2 v/v);
(□) in toluene/MeOH (13/2 v/v) (ligand/Cu values are indicated at the top of the Figure);
(o) for solutions of PS-Im with α=0.03 in the absence of copper ions in toluene/iso-propanol (13/2 v/v).

The specificity of the oxidative coupling polymerization of DMP catalyzed by Cu(II)-PS-Im complexes was studied in toluene/iso-propanol (13/2 v/v). Enhanced PPO formation is obtained with increasing ligand/copper ratio, as shown in Fig.5 for α=0.07, 0.11 and 0.23. A DPQ yield of only 5% is found for ligand/copper=10. So, the good specificity in case of Cu(II)-NMIm [8] is also observed for Cu(II)-PS-Im. Considering the spectroscopic results, it seems

obvious that the mononuclear Cu(II)-PS-Im complex with four ligands as catalyst precursor is more favourable for C-O coupling leading to PPO formation than dinuclear species (see Scheme 2).

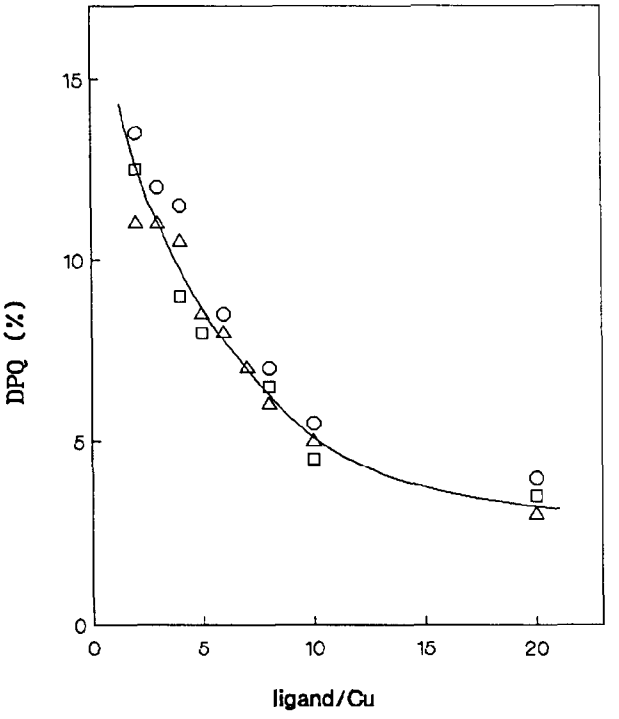


Fig.5 Effect of ligand/Cu ratio on final specificity under standard conditions for PS-Im with:
(□) α=0.07; (Δ) α=0.11; (o) α=0.23.

3.3.4 Effect of chain loading α

Fig.5 also shows that the specificity of Cu(II)-PS-Im is unaffected by the degree of loading α of the copolymers with imidazole ligands. This implies that the macromolecular chain itself does not influence the catalytic specificity, which was also observed in previous investigations with pyridine or DMAP-type ligands [4,13].

However, the effect of chain loading α on the reaction rate is pronounced, as shown in Fig.6 under standard conditions with ligand/copper=4 and 10. For both ratios a maximum in the reaction rate is found around α=0.11. This is in accordance with EPR spectroscopic results, which show that an

increase in α value up to α=0.11 gives an enhanced amount of $Cu(PS\text{-}Im)_4^{2+}$ and a decline of $Cu(PS\text{-}Im)_{1-3}^{2+}$ species. However, this is not appropriate to describe the maximum in the effect of α on the reaction rate. As reported by Schouten and Challa [14,15], strain in the polymer chain segments between neighbouring ligand groups may also play an important role in the effect of α on the activity of the catalyst. For copper(II) complexes of polymer-bound dimethylamine and pyridine, it was shown by Challa et al. [7,16] that the increase of the electron-transfer rate with increasing α is governed by an enhancement of the activation entropy ($\Delta S^{\ddagger}$), which overcompensates for the retarding effect of a simultaneously increasing activation enthalpy ($\Delta H^{\ddagger}$). This explanation was supported by statistical calculations of intermediate chain conformations and by measurement of the heat of complexation of copper(II) ions with polymeric ligands for varying α.

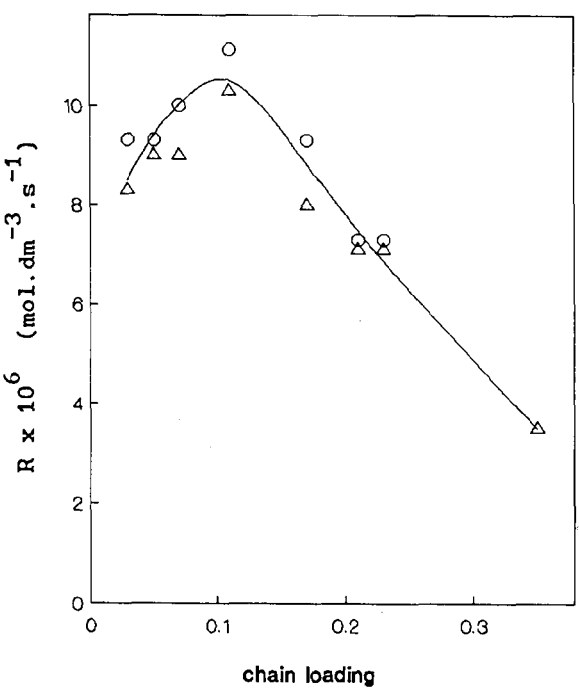


Fig.6 Steady state reaction rate as a function of chain loading α with imidazole ligands under standard conditions:
(Δ) ligand/Cu=4; (o) ligand/Cu=10.

It seems plausible that the above-mentioned explanation is also valid for the observed effect of α on the reaction rate in the present system. So, with increasing α the intermediate chain between neighbouring imidazole ligands becomes shorter and the strain in the catalyst increases. This causes an enhancement of $\Delta S^{\ddagger}$ for the electron transfer from substrate to copper(II).

When the intermediate chain between neighbouring imidazole ligands becomes too short, i.e. for α>0.11 in the present case, adjacent ligands can not coordinate to the same copper(II) ion any longer. In other words, one or more ligands have to be skipped over in favor of subsequent ones. Consequently, the strain in the polymer catalyst is reduced, resulting in a decreasing reaction rate. In fact, the skipped coordination of ligands to copper ions can be considered as a lowering of the "effective" value of α, which leads to lower reaction rate.

On the other hand, ligands skipped for steric reasons can coordinate with copper(II) ions attached to other sites on the same polymer backbone, which can be considered as a kind of intramolecular crosslinking. Besides, the smaller styrene group content of the polymer backbone for higher α may result in a reduced hydrophobicity around active centers. Both effects may reduce the accessibility of catalytically active sites for the substrate, which should have an extra retarding effect on the reaction rate.

3.3.5 Kinetics of oxidative coupling

Under standard conditions, reaction rates were measured for different DMP concentrations. So-called saturation kinetics are observed, as shown in Fig.7 (curve (Δ)). Therefore, the oxidative coupling polymerization of DMP catalyzed by Cu(II)-PS-Im complexes in toluene/iso-propanol can be described by a Michaelis-Menten mechanism as given in Scheme 3. In this scheme, E is the active copper(II) complex; E^{*} is the Cu(I) complex; $[E]_0$= overall concentration of copper salt; k_2= rate constant of rate-determining step; and $K_m=(k_{-1}+k_2)/k_1$ is the Michaelis-Menten constant.

From the double-reciprocal Lineweaver-Burk plot of reaction rate versus DMP concentration obeying the well-known equation:

$$\frac{1}{R} = \frac{1}{k_2[E]_0} + \frac{K_m}{k_2[E]_0[DMP]}$$

k_2 and K_m^{-1} (a measure of the accessibility of active site for DMP) have been calculated, yielding k_2=0.15 s^{-1} and K_m^{-1}=0.45 $dm^3.mol^{-1}$. Table 2 gives the values of k_2 and K_m^{-1} for both Cu(II)-NMIm and Cu(II)-PS-Im in different

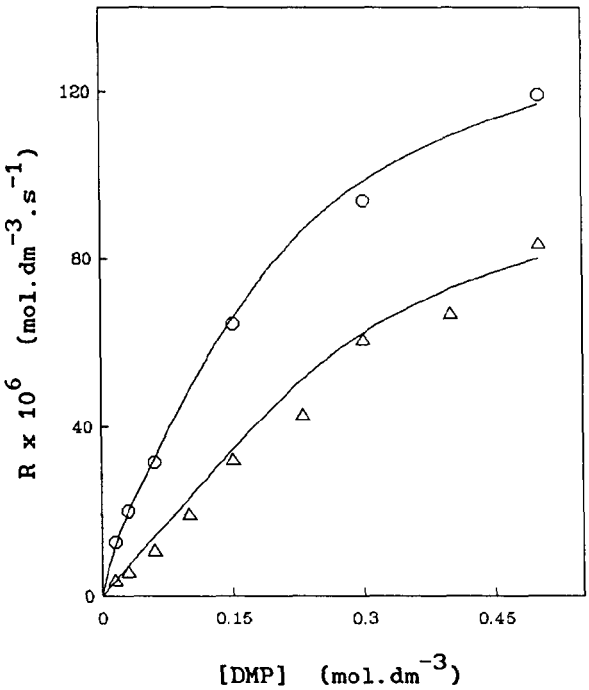
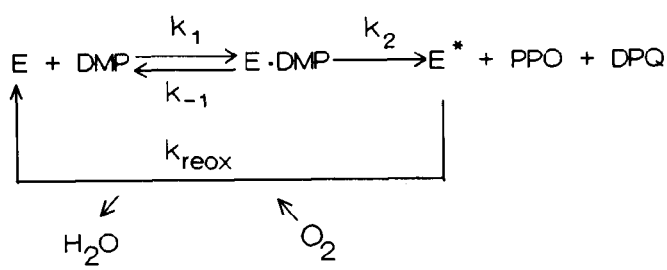


Fig.7 Steady state reaction rate as a function of initial DMP concentration under standard conditions: (Δ) adding base to Cu(II)-PS-Im for PS-Im with α=0.11; (o) adding base to DMP solution for PS-Im with α=0.07.



Scheme 3

solvent mixtures. An almost identical rate constant (k_2) of the rate-determining step is observed in all cases, which implies that the intrinsic activity of the catalyst depends mainly on the nature of the

imidazole ligand itself. However, the values of K_m^{-1} are much smaller for Cu(II)-PS-Im than for Cu(II)-NMIm in all solvent systems. In general, a higher local active center concentration in the polymer coils may enhance the K_m^{-1} value. On the contrary, steric hindrance of the polymer backbone and more difficult substitution of a polydentate ligand by substrate will have negative effects. In the present case of Cu(II)-PS-Im as catalyst, it seems that latter effects predominate and hamper the substitution of a polymeric ligand by substrate. The effect of solvent mixture on K_m^{-1} will be discussed later.

Notably, saturation kinetics in DMP was also found when adding the base to DMP solution, yielding phenolate anions (Fig.7, curve (o)), although the reaction rates were higher (see also Fig.2). This indicates that a phenolate anion-containing copper(II) complex is coordinated by a DMP molecule before the rate-determining step takes place.

3.3.6 Reaction order in [Cu(II)]

In the studies of polymer-bound DMAP copper(II) complexes as catalyst for the oxidative coupling polymerization of DMP, Koning et al. [17] suggested that dimerization of mononuclear copper complexes is necessary for the re-oxidation of Cu(I) to Cu(II). For constant amounts of polymeric ligands with α=0.17 and 0.05 ([imidazole]= 26.4 and 13.2 mmol.dm^{-3}, respectively),

Table 2. Kinetic parameters of oxidative coupling of DMP catalyzed by Cu(II)-NMIm and Cu(II)-PS-Im complexes under standard conditions

Complex	Solvent system (13/2 v/v)	Ligand/Cu	α	k_2 (s^{-1})	K_m^{-1} ($dm^3.mol^{-1}$)
Cu(II)-NMIm	toluene/iso-propanol	30	-	0.15	9.1
Cu(II)-NMIm	toluene/MeOH	30	-	0.15	12.5
Cu(II)-NMIm	ODCB/MeOH	30	-	0.12	12.6
Cu(II)-PS-Im	toluene/iso-propanol	4	0.11	0.15	0.45
Cu(II)-PS-Im	toluene/MeOH	4	0.17	0.15	1.69
Cu(II)-PS-Im	ODCB/MeOH	2	0.14	0.13	1.3 [6]

Fig.8 shows a first-order rate dependence on [Cu(II)] for log[Cu(II)]>-3.1 ([Cu(II)]>0.83 mmol.dm^{-3}) and a second-order rate dependence on [Cu(II)] for log[Cu(II)]<-3.1 ([Cu(II)]<0.83 mmol.dm^{-3}). This result indicates that, under standard conditions with [Cu(II)]=3.32 mmol.dm^{-3}, the local dimerization of

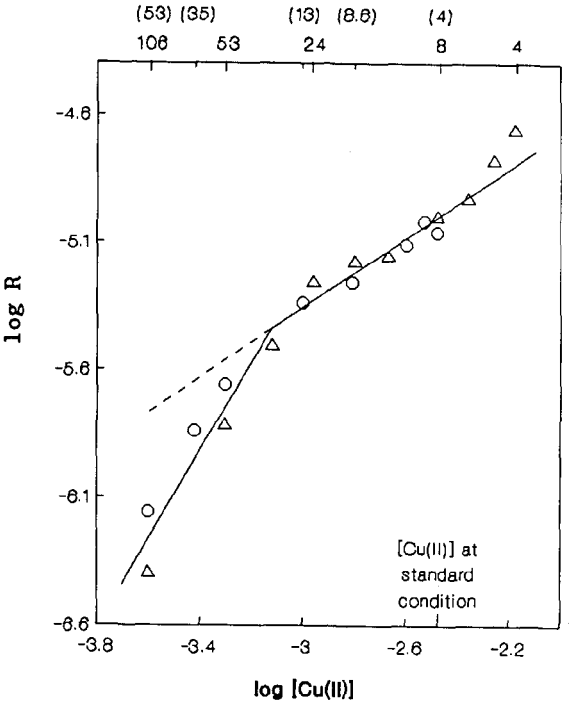


Fig.8 Plot of log R versus log [Cu(II)] under standard conditions for PS-Im with:
(Δ) α=0.17 and [imidazole]=26.6 mmol.dm^{-3};
(o) α=0.05 and [imidazole]=13.3 mmol.dm^{-3}.
Ligand/Cu values for α=0.17 are indicated at the top of the Figure; the values in parentheses are for α=0.05; R is the steady state reaction rate in mol.dm^{-3}.s^{-1}; [Cu(II)] in mol.dm^{-3}.

copper complexes is so fast that the oxidation rate of DMP (k_2) is rate-determining and the overall reaction is first-order in [Cu(II)]. On the contrary, for the low concentrations of copper(II) ions, the dimerization will become rate-determining. Then a second-order rate dependence on [Cu(II)] is observed. In the present case it appears that the transition from first to second order takes place at such [Cu(II)] that on the average only about one copper ion is present per polydentate coil. Consequently, dimerization will also be retarded because it often requires reaction between copper ions complexed in different polydentate coils.

3.3.7 Effect of solvent system on reaction rate

As shown in Fig. 9 the reaction rates with Cu(II)-PS-Im or Cu(II)-NMIm are

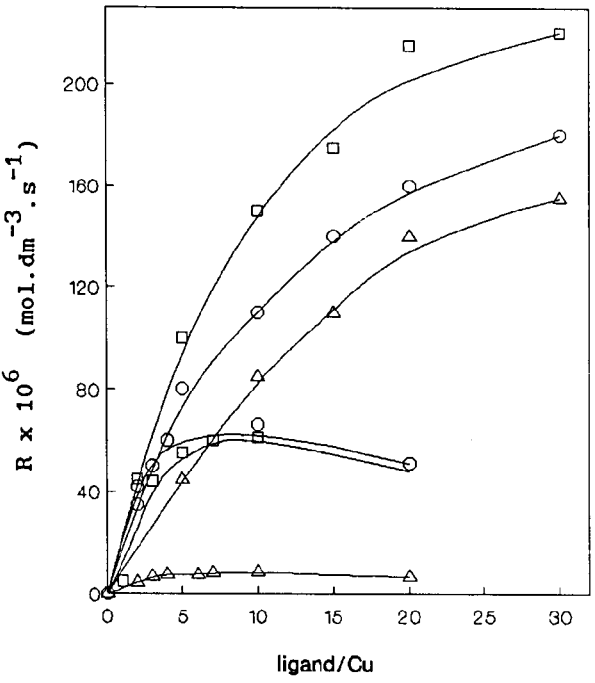


Fig. 9 Steady state reaction rate as a function of ligand/Cu ratio under standard conditions in different solvent systems.

For Cu(II)-NMIm: (Δ) toluene/iso-propanol (13/2 v/v);
(□) toluene/ MeOH (13/2 v/v);
(o) ODCB/MeOH (13/2 v/v).

For Cu(II)-PS-Im: (Δ) toluene/iso-propanol (13/2 v/v) and α=0.23;
(□) toluene/MeOH (13/2 v/v) and α=0.23;
(o) ODCB/MeOH (13/2 v/v) and α=0.17.

smaller for toluene/iso-propanol than for toluene/MeOH or ODCB/MeOH in the applied range of ligand/copper ratios. Table 2 also demonstrates that higher K_m^{-1} values are observed in toluene/MeOH or ODCB/MeOH than in toluene/iso-propanol. Obviously, this phenomenon is primarily related to either methanol or iso-propanol being used as cosolvent, rather than to expansion or

contraction of the polymeric ligands in solution. In fact, the same specific viscosities (η_{sp}) are observed for solutions of polymeric ligands in either toluene/MeOH or toluene/iso-propanol (see Fig.4). So, coordinated methanol seems to be more accessible to substitution by substrate than iso-propanol.

Fortunately, methanol gives only a slight decrease in catalytic specificity, i.e. under standard conditions with ligand/copper=10 for PS-Im with α=0.23, a DPQ yield of 7% is found in toluene/MeOH as compared to 5% in toluene/iso-propanol in Fig.5. Therefore, we prefer to use toluene/MeOH (13/2 v/v) as solvent mixture in future studies on immobilized polymer-bound imidazole copper(II) complexes.

3.4 References

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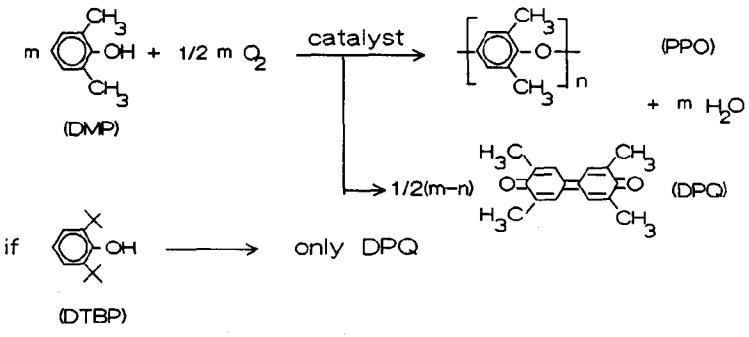
Chapter 4

Immobilization of Copper(II) Complexes of Poly(styrene-co-N-vinylimidazole) by Quaternization or Adsorption on Silica and their Catalysis of Oxidative Coupling of 2,6-Disubstituted Phenols

Abstract: Copper(II) complexes of poly(styrene-co-N-vinylimidazole) (Cu(II)-PS-Im) were immobilized on modified silica by quaternization or on unmodified silica by adsorption and these immobilized polymer-bound complexes were applied as catalysts for oxidative coupling polymerization of 2,6-dimethylphenol (DMP) in toluene/methanol (13/2 v/v). Higher average chain loading (α) of PS-Im with imidazole groups, e.g. $\alpha \geq 17\%$, was essential for successful adsorption. A main role of hydroxide appears to be production of the reactive phenolate anions from DMP. A rise in reaction rate was not observed for high ligand/Cu, which probably resulted from too high viscosity of the silica suspension at high ligand/Cu. In a batch process under comparable conditions both types of immobilized polymeric catalysts were found to have the same preference for poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) formation as non-immobilized Cu(II)-PS-im and their low molar mass analogue. However, they were five times less active than non-immobilized ones, which was explained primarily in terms of a reduced effective ligand/Cu ratio after the immobilization of polymeric ligands. Application of both types of immobilized polymeric catalysts in a continuous stirred tank reactor (CSTR) for oxidative coupling of 2,6-di-tert-butylphenol (DTBP) was successful. A stable phenol conversion was obtained in CSTR under suitable conditions for at least 120 hours.

4.1 Introduction

Immobilization of soluble polymer-bound catalysts on an inert support, combining the advantages of both homogeneous and heterogeneous catalysts, is expected to be a reliable technique to obtain effective catalysts for industrial applications. In this laboratory the oxidative coupling of 2,6-disubstituted phenols (Scheme 1) catalyzed by copper(II) complexes of immobilized polymer-bound pyridine or 4-dimethylaminopyridine (DMAP) has been extensively studied [1-3]. In view of the lower intrinsic activity and specificity of the pyridine-based catalysts [4] and excessively strong



Scheme 1

basicity of DMAP ligands [3], these catalysts were not suitable for continuous processes. On the other hand, copper(II) complexes of imidazole ligands with mild basicity [5] possess higher intrinsic activity than complexes with pyridine [6,7]. This has prompted us to study the immobilized polymer-bound imidazole copper(II) complexes as catalysts for the applied reaction.

Recently, we investigated copper(II) complexes of N-methylimidazole (Cu(II)-NMIm) [8] and Cu(II)-PS-Im [9] as catalysts (Fig.1, type a and b, respectively) for the oxidative coupling polymerization of DMP. In both cases

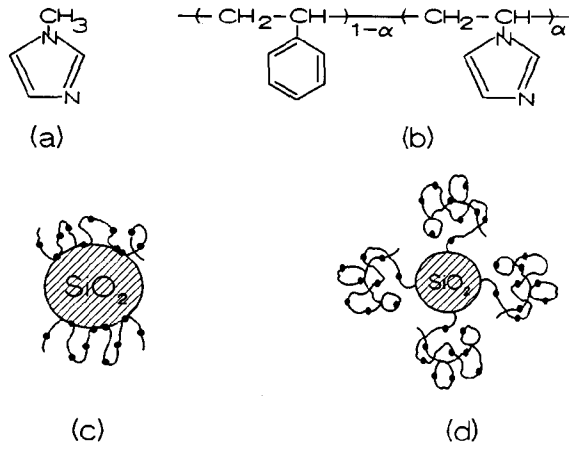


Fig.1 Schematic representation of free and immobilized imidazole ligands in copper(II) complexes as catalysts: (a) NMIm; (b) PS-Im; (c) silica-quaternized or adsorbed PS-Im; (d) silica-grafted PS-Im.

mononuclear Cu(imidazole)$_4^{2+}$ species present at high ligand/Cu were found to be the better catalyst precursors and more favourable for PPO formation than dinuclear complexes. In addition, toluene/methanol (13/2 v/v) appeared to be a suitable solvent mixture for obtaining both high activity and good specificity.

In this paper we report on the immobilization of polymeric ligands on silica by quaternization or by the very simple adsorption approach reported before [10,11]. Compared with free Cu(II)-NMIm and Cu(II)-PS-Im some similarities as well as differences will be discussed in catalytic behaviour of both immobilized Cu(II)-PS-Im complexes (Fig.1, type c) for the oxidative coupling polymerization of DMP in toluene/methanol (13/2 v/v) with a batch-type reactor. Moreover, the application of these immobilized polymeric catalysts in a continuous process for oxidative coupling of DTBP will be described.

4.2 Experimental

4.2.1 Materials

$CuCl_2(H_2O)_2$ (analytically pure), KOH and methanol (Uvasol, Merck) were used as received. N-vinylimidazole and styrene (Aldrich) were distilled from KOH under reduced N_2 atmosphere. DMP (Aldrich) was purified by repeated recrystallization from n-hexane. DTBP (Janssen) was used without further purification. Toluene (Merck) was dried over Na. The non-porous Aerosil OX50 (specific surface 50 $m^2.g^{-1}$, average sphere diameter 50 nm) containing $2.5x10^{18}$ "-SiOH" groups per square metre was kindly provided by Degussa AG. All silane compounds (Janssen) were used directly.

4.2.2 Synthesis and characterization of applied PS-Im

Radical copolymerization of N-vinylimidazole and styrene was performed in toluene using AIBN as an initiator. Synthesis and characterization of PS-Im were reported in *Chapter 3*.

4.2.3 Quaternization procedure

Modification of Aerosil OX50 with alkoxysilanes was carried out in toluene under N_2 at reflux temperature (Fig.2). After 24 hours half of the toluene was distilled off. Then the residue was centrifuged, washed twice, dried in high vacuum at 60 ^oC for 3 days and characterized by elemental analysis. Some of samples were further treated with $EtOSi(CH_3)_3$ in toluene

(Fig.2) by the same experimental procedure as mentioned above. The results for different samples are listed in Table 1.

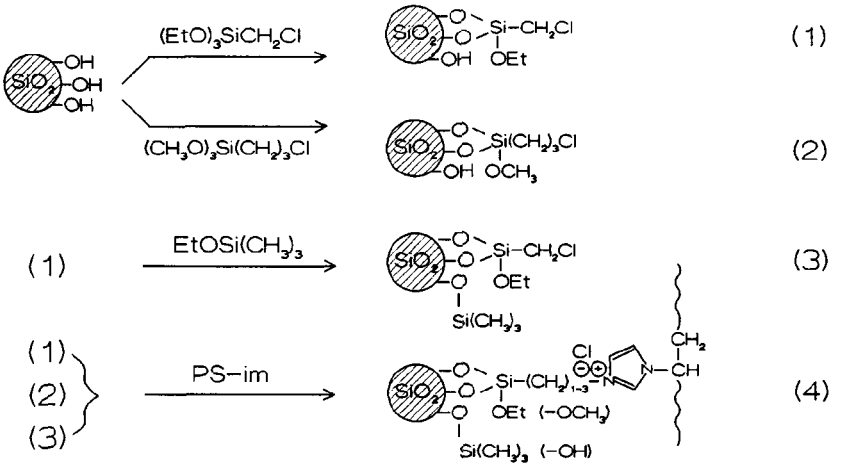


Fig.2 Immobilization of PS-Im on silica by quaternization.

Table 1. Modification of Aerosil OX50 with alkoxysilanes[a)]

Samples	Alkoxsilanes	(mmol/g.Aer.)	$EtOSi(CH_3)_3$	% Cl
Aerosil OX50	-	0	no	0
A'	$(EtO)_3SiCH_2Cl$	0.1	excess	0.22
B'	$(EtO)_3SiCH_2Cl$	0.01	excess	0.11
C'	$(EtO)_3SiCH_2Cl$	0.005	excess	0.025
D'	$(EtO)_3SiCH_2Cl$	0.005	no	0.03
E'	$(CH_3O)_3Si(CH_2)_3Cl$	0.125	no	0.18

a) **Reactions were carried out in toluene under N_2 at reflux temp. for about 24 hours.**

Quaternization of PS-Im on modified Aerosil OX50 was also performed in toluene (Fig.2). For example, 3 gram of modified Aerosil OX50 was suspended in 60 ml toluene and 2 gram of PS-Im was added to this suspension. The solution was stirred under N_2 at 60 ^{o}C for 3 days. Subsequently, the loaded silica particles were centrifuged and the upper layer was decanted. The residue was suspended in 30 ml chloroform with stirring for 24 hours, then again

centrifuged and decanted. This procedure was repeated 3 times in order to remove unbound and entangled copolymer chains. The product obtained was dried (as above) and characterized by elemental analysis. The results are compiled in Table 2.

Table 2. Quaternization of PS-Im on modified Aerosil OX50[a)]

samples	used materials		α[b)]	θ[c)]	β[d)]	$k_{obs}x10^3$ [e)]	DPQ[e)]
		(%Cl)	(%)	(%)	(%)	(s^{-1})	(%)
A	A'	(0.22)	12	5.9	90	4.0	10
B	B'	(0.11)	12	5.8	46	3.8	9.0
C	C'	(0.025)	12	5.6	11	1.6	11
D	D'	(0.03)	12	7.2	10	3.3	12
E	E'	(0.18)	17	3.8	80	3.1	11

a) Reactions were carried out in toluene under N_2 at 60°C for 72 hours.

b) Chain loading of used PS-Im with imidazole groups.

c) Loading degree of silica: wt.% of PS-Im on Aerosil OX50.

d) Maximum percentage of imidazole groups of PS-Im that could react with all chloromethyl groups on modified Aerosil OX50; it can be deduced that: $\beta=\%Cl x[104(1-\alpha)+94\alpha]/(35.5x\alpha x\theta)$.

e) From catalytic experiments taken under standard conditions; $k_{obs}\equiv R/[CuCl_2]_0$ assuming that all $CuCl_2$ yield active catalyst.

4.2.4 Adsorption procedure

5 gram of Aerosil OX50 was suspended in 60 ml toluene/methanol (13/2 v/v) and 0.5 gram of PS-Im was added. This solution was gently shaken at 25 °C for 24 hours. Subsequently, the loaded silica particles were centrifuged (decanting the upper layer) and resuspended in another 60 ml toluene/methanol (13/2 v/v) containing 0.5 gram of fresh PS-Im. Again the suspension was gently shaken at 25 °C for 24 hours. This procedure was repeated 3 times in order to have the high molar mass components of heterodisperse copolymer immobilized by the preferential adsorption of longer polymer chains [12,13]. This should be more favourable for the catalytic activity because of the presence of longer loops and tails in case of longer adsorbed polymer chains [14]. Then weakly adsorbed and entangled polymer chains were removed by suspending and shaking the loaded silica particles twice in the same solvent mixture at 25 °C for 24

hours. The residue was centrifuged, dried (as above) and characterized by elemental analysis. Fig.3 illustrates the adsorption interactions and Table 3 gives all results for different samples.

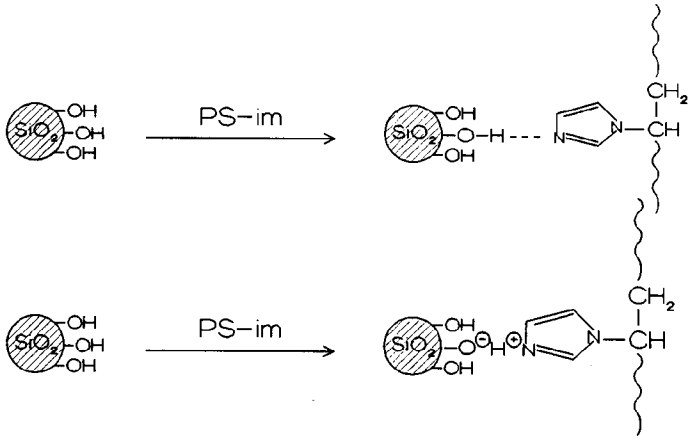


Fig.3 Immobilization of PS-Im on silica by adsorption.

Table 3. Adsorption of PS-Im on Aerosil OX50[a)]

samples	α (%) [b)]	θ (%) [c)]	k_{obs}x10^3 (s^{-1}) [d)]	DPQ (%) [d)]
P	5	0	-	-
Q	12	0	-	-
R	17	2.7	2.8	13
S	35	9.5	4.1	14

a) **Reactions were carried out in toluene/methanol (13/2 v/v) at 25°C for 72 hours.**

b) **Chain loading of used PS-Im with imidazole groups.**

c) **Loading degree of silica: wt.% of PS-Im on Aerosil OX50.**

d) **From catalytic experiments taken under standard conditions.**

4.2.5 Oxidative coupling in a batch-type reactor

The oxidative coupling polymerization of DMP was carried out in a round-bottomed flask with stirring, instead of shaking of the cylindrical reaction vessel [9], to prevent loaded silica particles from sticking on the top wall of the vessel. Immobilized polymeric catalysts were prepared in situ by suspending the Aerosil OX50-quaternized or adsorbed polymer-bound imidazole

ligands in toluene and adding $CuCl_2$/methanol solution. The coordination equilibrium period was taken to be about 24 hours. After saturating the reaction system with O_2 the reactions were started by adding hydroxide (as KOH dissolved in methanol) and DMP, subsequently. Steady state reaction rates R were obtained by measuring O_2 uptake as a function of time with an automatic isobaric gas burette. Relative observed reaction rates (k_{obs}) for a definite substrate concentration were calculated as $k_{obs} \equiv R/[CuCl_2]_0$ assuming that all $CuCl_2$ yield active catalyst. The stirring speed for the reaction solution was high enough to prevent gas-liquid diffusion of O_2 becoming rate determining. The following standard conditions were applied: T= 25 °C; Po_2= 101.3 kPa; [DMP]= 0.06 mol.dm^{-3}; [Cu(II)]= 0.33x[OH^-]= 0.25x[imidazole]= 0.83 mmol.dm^{-3}; total solvent mixture, toluene/methanol (13/2 v/v), 0.015 dm^3.

4.2.6 Oxidative coupling in CSTR

Fig.4 shows the continuous reaction set-up for oxidative coupling. The

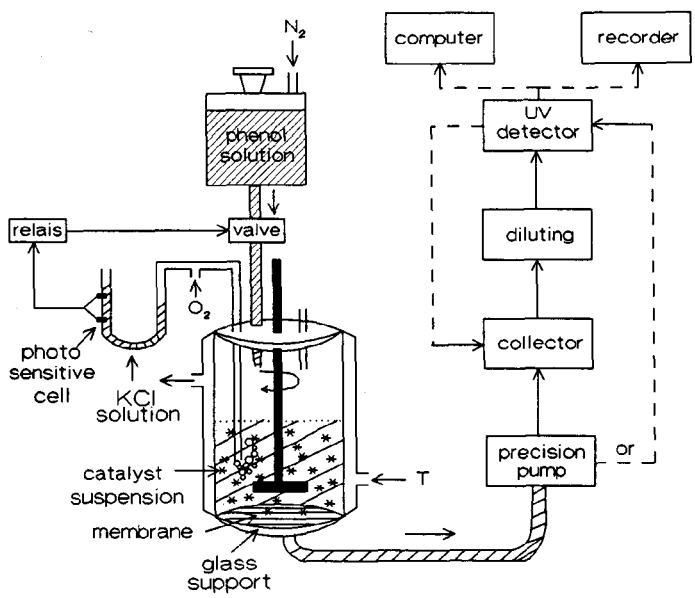


Fig.4 Schematic drawing of the apparatus for continuous oxidative coupling process of phenols catalyzed by silica-immobilized Cu(II)-PS-Im.

diameter of pores in the applied PTFE membrane is 20 nm. Leaching of Cu(II)

from the polydentate coil as well as detachment of immobilized polymeric ligands from silica appeared to be negligible [3]. The standard conditions were: T= 25 ^{o}C; Po_2= 101.3 kPa; $[DTBP]_0$= [DTBP]= 0.02 mol.dm^{-3}; $[Cu(II)]_0$= 0.5x$[imidazole]_0$= 0.21 mmol.dm^{-3}; total solvent mixture, toluene/methanol (13/2 v/v), 0.15 dm^3; flow rate, 0.2 cm^3.min^{-1}. The coordination equilibrium period was taken to be about 24 hours and was followed by an addition of hydroxide as KOH dissolved in methanol.

4.2.7 Measurement of the concentrations of DPQ

In batch-type experiments, once the reaction was complete the reaction mixture was immediately diluted with chloroform and subsequently the overall catalytic specificity was determined by measuring the concentrations of the side product DPQ with a PYE Unicam SP-8-200 UV/VIS Spectrophotometer at 421 nm (ε=74,000 dm^3.mol^{-1}.cm^{-1}) because PPO and DPQ are practically the sole products from DMP.

For continuous experiments, DTBP was used as a substrate since it yields only one main product, viz. its DPQ (Scheme 1), which could be continuously detected by UV/VIS spectrophotometry at 426 nm (ε=65,000 dm^3.mol^{-1}.cm^{-1}) after strong dilution with chloroform. From these data the stability of the catalyst could be derived.

4.3 Results and Discussion

4.3.1 Quaternization of PS-Im and catalysis of their Cu(II) complexes

If one assumes that all chloromethyl groups on modified silica have taken part in the quaternization one can expect, from the values of β in Table 2, that the catalytic activities should increase in the order sample C > sample B > sample A, because only 10% of the imidazole groups of PS-Im in sample A would be available for coordination with Cu(II) and formation of the catalyst precursor. However, the catalysis results in Table 2 fail to support this assumption. Therefore, it is concluded that part of the chloromethyl groups on modified silica, especially in the case of the sample with the high chlorine content, does not take part in quaternization with imidazole groups of PS-Im, e.g. for two neighbouring chloromethyl groups only one participates in quaternization.

On the other hand, further hydrophobic silanization of the silica surface does not improve the catalytic activity (comparing sample C with sample D in Table 2) in contrast with the situation described by Verlaan et al for

silica-grafted pyridine-based polymeric catalyst [15]. Besides, sample E in Table 2 with a longer spacer between the chloromethyl group and the silica surface gives about the same catalytic activity.

Finally, the catalytic specificity (%DPQ) is about the same for all samples, while the catalytic activity deviates only for sample C. The reason for this deviation is not clear since α and θ are equal to those for sample A and B.

4.3.2 Adsorption of PS-Im on silica

As shown in Table 3 the loading degree (θ) for sample S with α=35% is higher than that for sample R with α=17%, whereas no adsorption takes place at all for samples with α=5 and 12% (sample P & Q). This result can be explained in terms of thermodynamics. In general, adsorption of polymer chains is an entropy-lowering process ($\Delta S<0$). So, a negative adsorption free energy ΔG can be achieved only by means of more hydrogen bond (and/or acid-base) interactions (Fig.3) yielding a more negative ΔH. This implies that the chain loading (α) of PS-Im with imidazole groups should be higher than a critical value (α^*) in order to get stable adsorption. In addition, one should remember that PS-Im still has a distribution of α values although the conversions of all copolymerizations were kept below 15% [9]. Therefore, the higher value of θ obtained for sample S with α=35% than for sample R with α=17% might indicate that α^* is probably higher than the average value of α=17% for sample R. So, only the fraction with $\alpha>\alpha^*$ can give stable adsorption on silica surfaces.

4.3.3 Effect of chain loading of PS-Im

The optimum value of α=12% for a maximum reaction rate as found in toluene/iso-propanol (13/2 v/v) for non-immobilized Cu(II)-PS-Im [9] is also observed in the present case in toluene/methanol (13/2 v/v) (Fig.5), although all reaction rates are higher than those in the toluene/iso-propanol mixture. The effect of chain loading α of PS-Im with imidazole groups on catalytic activity was discussed in a previous paper [9] in terms of strain in the polymer chain segments between neighbouring imidazole ligand groups [16.17]. However, after immobilization of PS-Im on silica by adsorption a higher catalytic activity is found for α=35% than for α=17% as shown in Table 3. It is understandable that participation of many imidazole groups of PS-Im in the adsorption process causes the effective chain loading for complexation of copper(II) ions to decrease, so that the optimum overall α shifts to higher value.

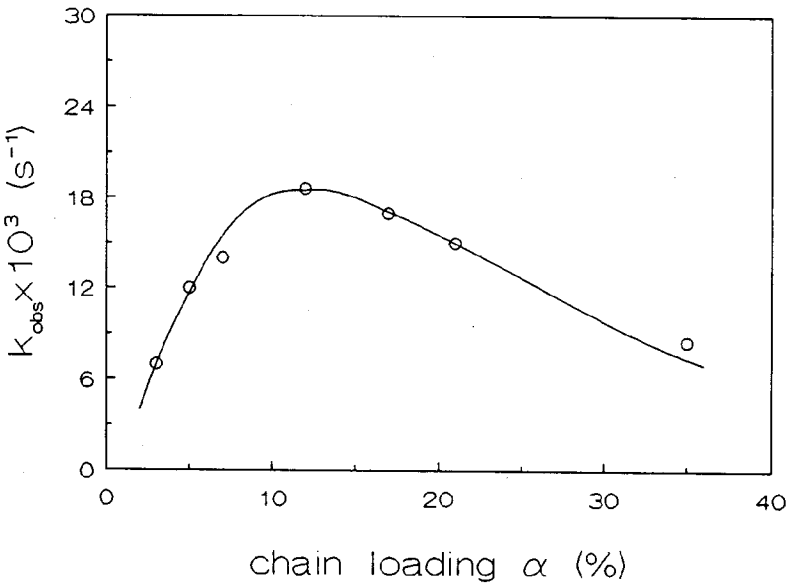


Fig.5 Effect of chain loading on reaction rate for free Cu(II)-PS-Im as catalyst under standard conditions with $[Cu(II)] = [OH^-] = 0.25x[imidazole] = 3.32$ mmol.dm^{-3}.

4.3.4 The role of hydroxide

Table 4 shows that with immobilized polymeric catalysts no reaction takes place in the absence of base as was also found in the cases of non-immobilized Cu(II)-NMIm [8] and Cu(II)-PS-Im [9]. However, now a maximum reaction rate for silica-quaternized Cu(II)-PS-Im is observed at OH/Cu=3 instead of OH/Cu=1 and 2 for free Cu(II)-NMIm and Cu(II)-PS-Im, respectively. Apparently, on immobilizing homogeneous Cu(II)-PS-Im complexes on silica their stability against base improves. The main role of base in the case of immobilized polymeric catalysts is still to produce the reactive phenolate anions from DMP [18-20], whereas an excess of hydroxide somehow causes catalyst destruction [8,9].

In case of silica-adsorbed Cu(II)-PS-Im still higher reaction rates are found with increasing OH/Cu up to 5 (Table 4). A control experiment under the same conditions in the absence of $CuCl_2$ and DMP indicated that desorption of PS-Im from the silica surface takes place at this high base concentration. Consequently, at OH/Cu=5 the same reaction rate was observed as for free Cu(II)-PS-Im at OH/Cu=1 under comparable conditions. However, the steady state

reaction rates for OH/Cu>4 lasted only a very short period and were followed by a sharp reduction of O_2 consumption rates due to the fact that the desorbed catalysts were destroyed. On the other hand, some consumption of hydroxide by the acidic silanol groups on unmodified silica surface might also result in a shift of the optimum OH/Cu to higher value.

Table 4. Effect of OH/Cu on catalysis under standard conditions

catalysts	OH/Cu	$k_{obs} x10^3$ (s^{-1})	DPQ (%)
Aerosil OX50-	0	0	-
quaternized	1	1.2	10
Cu(II)-PS-Im	2	1.9	11
(sample B)	3	3.8	9.0
	4	2.7	11
Aerosil OX50-	0	0	-
adsorbed	3	4.1	14
Cu(II)-PS-Im	4	(8.5)*	12
(sample S)	5	(20)*	11

*** Values lasting for only very short times, because desorption and catalyst destruction take place.**

4.3.5 Effect of ligand/Cu

In previous studies with non-immobilized catalyst systems we found higher reaction rates for higher ligand/Cu ratios because of the formation of more mononuclear $Cu(imidazole)_4^{2+}$ species. Enhancement of reaction rates was obtained even for ligand/Cu>30 in case of Cu(II)-NMIm [8] but only up to 10 in case of Cu(II)-PS-Im due to the overlap of polymer coils in solution [9]. However, such an effect is not observed for both immobilized polymeric catalysts present (Table 5). In fact, owing to the relative low loading degrees (θ<10%) for all immobilized polymeric catalysts, high ligand/Cu would require a large number of loaded silica particles in only 15 ml solvent mixture (standard condition). Then, the high viscosity of the silica suspension probably limits diffusion of reactants. Therefore, with silica-quaternized or adsorbed Cu(II)-PS-Im as catalysts no increase of reaction rate is observed for ligand/Cu>2. In both cases identical %DPQ is found irrespective of the applied ligand/Cu ratios (Table 5). This differs from the cases of free Cu(II)-NMIm [8] and Cu(II)-PS-Im [9], wherein

increasing ligand/Cu is always accompanied by a decrease in %DPQ resulting from the transformation of binuclear copper complexes into mononuclear species.

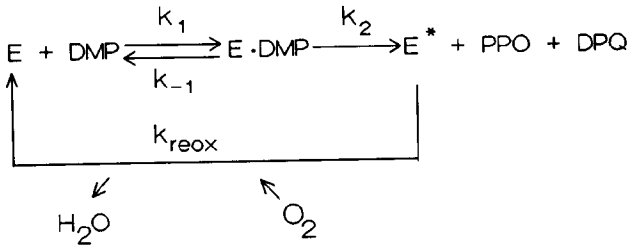
Table 5. Effect of ligand/Cu on catalysis under standard conditions

catalysts	ligand/Cu	$k_{obs} x10^3$ (s^{-1})	DPQ (%)
Aerosil OX50-	**0**	**0**	**-**
quaternized	**1**	**4.1**	**11**
Cu(II)-PS-Im	**2**	**5.8**	**12**
(sample B)	**4**	**3.8**	**9.0**
Aerosil OX50-	**1**	**1.3**	**14**
adsorbed	**2**	**2.8**	**12**
Cu(II)-PS-Im	**4**	**2.8**	**13**
(sample R)			

4.3.6 Kinetics of oxidative coupling

We investigated the kinetics of oxidative coupling polymerization of DMP catalyzed by Aerosil OX50-adsorbed Cu(II)-PS-Im. Under standard conditions so-called saturation kinetics are observed and the double-reciprocal Lineweaver-Burk plot of reaction rate versus DMP concentration is given in Fig.6. A straight line intersects the Y axis in agreement with the well-known equation:

$$\frac{1}{R} = \frac{1}{k_2[E]_0} + \frac{K_m}{k_2[E]_0[DMP]}$$



Scheme 2

Therefore, this reaction can be described by a Michaelis-Menten mechanism as

given in Scheme 2.

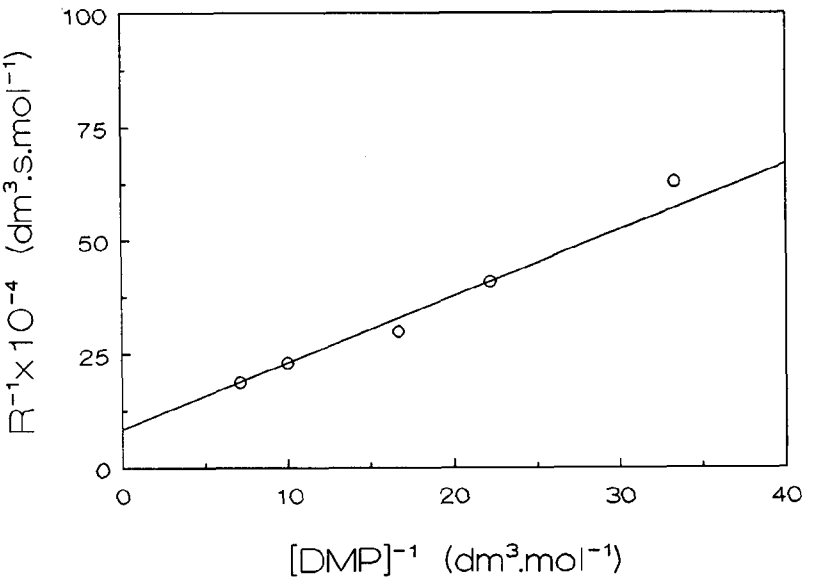


Fig.6 Double reciprocal Lineweaver-Burk plot of steady state reaction rate versus substrate concentration under standard conditions for Aerosil OX50-adsorbed Cu(II)-PS-Im (sample S) as catalyst.

E is the active Cu(II)-PS-Im complex; E^* is the Cu(I) complex; $[E]_0$= overall concentration of the active Cu(II) ions; k_2= rate constant of rate-determining step; $K_m=(k_{-1}+k_2)/k_1$ (the Michaelis-Menten constant). From the straight line in Fig.6 k_2 and K_m^{-1}, a measure of the accessibility of active sites for substrate, have been calculated yielding k_2= 0.014 s^{-1} and K_m^{-1}= 5.8 $dm^3.mol^{-1}$. These values imply that the reduction in reaction rate, after immobilization, compared to that for non-immobilized Cu(II)-PS-Im with k_2= 0.15 s^{-1} and K_m^{-1}= 1.7 $dm^3.mol^{-1}$, is mainly caused either by a decrease of the intrinsic activity of catalytic sites (k_2), or by a decrease of $[E]_0$ ($[E]_0<[CuCl_2]_0$) due to incomplete transformation of $CuCl_2$ into active complex. A similar difference in k_2 was found by Koning et al [3] for non-immobilized and Aerosil 200V-grafted Cu(II)-PS-DMAP catalyzing the oxidative coupling polymerization of DMP in 1,2-dichlorobenzene/methanol (ODCB/MeOH) (13/2 v/v). Exceptionally, identical k_2 values were observed by Verlaan et al [1] for free and Aerosil 200V-grafted Cu(II)-PS-pyridine as catalysts for oxidative

coupling of DTBP in ODCB/MeOH (13/2 v/v), which probably can be attributed to the very low intrinsic activities of $k_2 \simeq 0.02\ s^{-1}$ in these cases.

4.3.7 Comparison of different catalytic systems

Table 6 demonstrates that immobilization of polymeric imidazole ligands on silica does not affect the catalytic specificity (%DPQ) of their Cu(II) complexes. However, relative observed reaction rates (k_{obs}) for both silica-quaternized and adsorbed Cu(II)-PS-Im as catalysts are five times lower than for non-immobilized ones. A few reasons can be considered:

First, water enrichment owing to free hydrophilic silanol groups on the silica surface in case of the adsorbed catalyst can probably reduce the catalytic activity [15]. This interpretation was not supported by the hydrophobic modification of silica with "$EtOSi(CH_3)_3$" in case of quaternized catalyst (Table 2). However, another possibility for water enrichment in the latter case might be the ion-pair formation on the silica surface due to the quaternization reaction (Fig.2). But, this explanation is not in agreement with the experimental results of Tsuchida et al. for non-immobilized partially-quaternized polyvinylpyridine copper complexes as catalysts for the oxidative coupling polymerization of DMP [19].

Consequently, the reductions in reaction rate after immobilization are believed to be primarily caused by the decrease of effective ligand/Cu because part of the imidazole ligands have taken part in the quaternization or adsorption processes and still higher overall ligand/Cu ratios can not be applied because of excessively high viscosity of the silica suspension. The shortage of available imidazole ligands is unfavourable for the complete formation of the mononuclear $Cu(imidazole)_4^{2+}$ species [8,9], which might result in a reduced k_2. On the other hand, in case of the immobilized polymeric catalyst, the incomplete transformation of $CuCl_2$ into an active complex, yielding $[E]_0 < [CuCl_2]_0$, probably also results in a decrease of k_2 as mentioned above.

Finally, in comparing imidazole-based catalysts with pyridine or DMAP-based ones under proper conditions (Table 6), the present catalytic systems show better catalytic specificity and intermediate catalytic activity. The higher reaction rate for grafted DMAP-based catalyst than for the adsorbed one indicates that immobilization by grafting is a better approach to obtain more effective catalyst although the grafting method is more laborious than adsorption or quaternization [1]. We shall report on Aerosil 200V-grafted Cu(II)-PS-Im as catalysts (Fig 1, type d) in a next paper [21].

Table 6. Comparison of catalysis for different catalytic systems under comparable conditions

catalysts	ligand/Cu	OH/Cu	$k_{obs} x10^3$ (s^{-1})	DPQ (%)
Cu(II)-NMIm	4	1	21	14
Cu(II)-PS-Im	4	1	19	15
Aerosil OX50-quaternized Cu(II)-PS-Im (sample A)	4	3	4.0	10
Aerosil OX50-adsorbed Cu(II)-PS-Im (sample S)	4	3	4.1	14
Aerosil 200V-grafted Cu(II)-PS-py (α=25%; θ=38%)[a]	2	1	<1.0	>40[b]
Aerosil 200V-adsorbed Cu(II)-PS-DMAP (α=28%; θ=14%)[c]	4	1	3.4	29
Aerosil 200V-grafted Cu(II)-PS-DMAP (α=30%; θ=28%)[c]	4	1	16	19

a) In ODCB/MeOH (13/2 v/v) and for [DTBP]=0.18 mol.dm^{-3} [2].

b) For non-immobilized Cu(II)-PS-pyridine in ODCB/MeOH (13/2 v/v) [4].

c) In ODCB/MeOH (13/2 v/v) [3].

4.3.8 Stability of immobilized catalysts

Aerosil OX50-quaternized Cu(II)-PS-Im has been applied as catalyst for the oxidative coupling of DTBP in a continuous stirred tank reactor as shown in Fig. 4. Under standard conditions with $(OH/Cu)_0$=1.5 a stable DTBP conversion is observed for at least 120 hours as shown in Fig. 7. This result not only demonstrates the successful application of an immobilized polymeric catalyst in continuous process but also confirms that phenolate anions, produced from initial hydroxide and DTBP, are regenerated during the oxidative coupling reaction and do not escape from the catalytic intermediate. This fact should be taken into account when considering the mechanism of oxidative coupling of phenols catalyzed via Cu(II)-amine complexes.

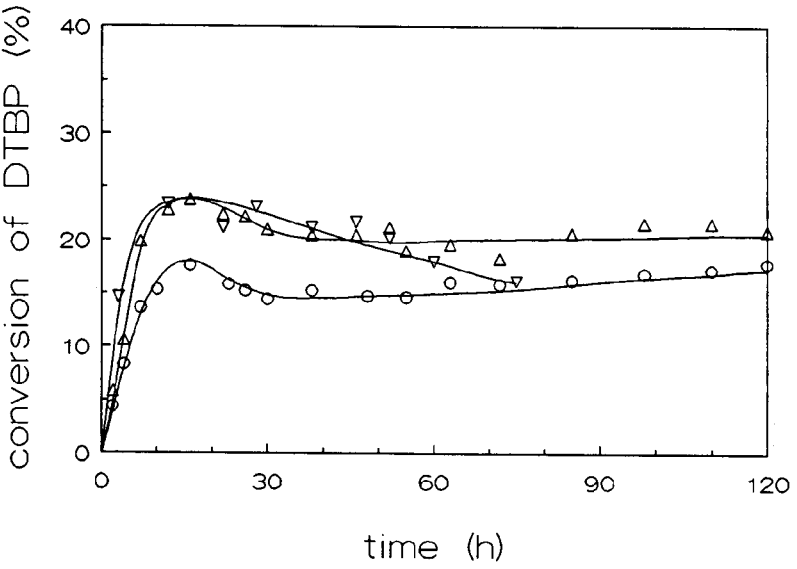


Fig.7 Stability of Aerosil OX50-quaternized Cu(II)-PS-Im (sample A) as catalyst for oxidative coupling of DTBP in a CSTR under standard conditions: (o) $(OH/Cu)_0$=1 and flow rate, 0.2 ml/min; (Δ) $(OH/Cu)_0$=1.5 and flow rate, 0.2 ml/min; (∇) $(OH/Cu)_0$=3 and flow rate, 0.4 ml/min.

In Fig.7 the lower initial DTBP conversion for $(OH/Cu)_0$=1, compared with the case of $(OH/Cu)_0$=1.5, results from the presence of a smaller number of reactive phenolate anions. The slight gradual rise in this conversion seems to imply a structural optimization with time of the catalytic sites containing phenolate anions. Anyhow, $(OH/Cu)_0$=1.5 seems to be more favourable for an optimum activity than $(OH/Cu)_0$=1, maybe because of loss of a small amount of hydroxide at the beginning of the reaction. However, the decreasing conversion in case of $(OH/Cu)_0$=3 as also shown in Fig.7 indicates that still higher initial base concentrations are not suitable anymore for a continuous catalytic process, probably because of destruction of catalysts by base at high OH/Cu ratios during a long period.

Similar catalytic stabilities of Aerosil OX50-adsorbed Cu(II)-PS-Im were obtained for $(OH/Cu)_0$= 1 and 1.5 as shown in Fig.8. This indicates that desorption of the polymer-bound catalyst from the silica surface does not take place, indeed. Finally, an experiment without added hydroxide pointed out that small amounts of phenolate anions may be formed, which give rise to DTBP

conversion values of only 3-5% after 20-150 hours. So, initial addition of base remains favourable for good yields.

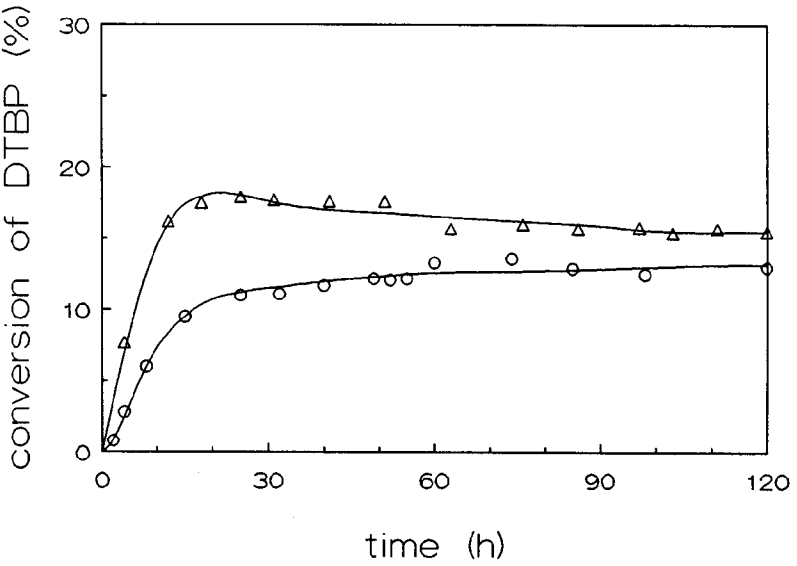


Fig.8 Stability of Aerosil OX50-adsorbed Cu(II)-PS-Im (sample S) as catalyst for oxidative coupling of DTBP in CSTR under standard conditions: (o) $(OH/Cu)_0$=1; (Δ) $(OH/Cu)_0$=1.5.

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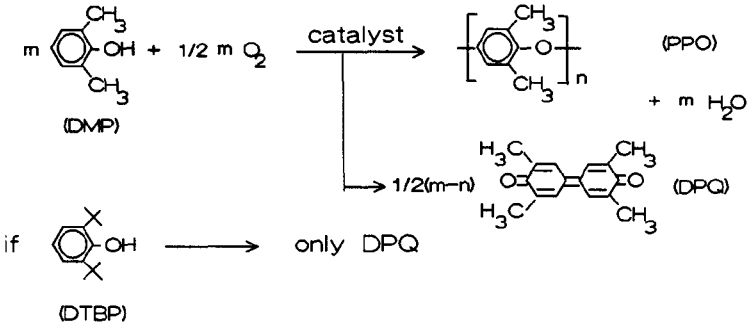
Chapter 5

Immobilization of Copper(II) Complexes of Poly(styrene-co-N-vinylimidazole) by Grafting on Silica and their Catalysis of Oxidative Coupling of 2,6-Disubstituted Phenols

Abstrac: Copper(II) complexes of poly(styrene-co-N-vinylimidazole) (Cu(II)-PS-Im) were immobilized on modified silica by radical graft copolymerization of N-vinylimidazole and styrene and characterized by VIS and EPR spectrometry. In this graft copolymerization, the same reactivity ratios were found as obtained from non-graft copolymerization initiated by AIBN, i.e. r_1=0.07 and r_2=7.0 for N-vinylimidazole and styrene, respectively. In a batch process under comparable conditions, these Cu(II)-PS-Im complexes grafted on silica are catalytically more active for oxidative coupling of 2,6-dimethylphenol (DMP) in toluene/methanol (13/2 v/v) than those immobilized on silica by quaternization or adsorption. However, they are three times less active than non-immobilized Cu(II)-PS-Im or their low molar mass analogue for ligand/Cu=4, which is primarily attributed to a non-optimum Cu(II) complex formation. Decreasing reaction rates for still higher ligand/Cu ratios probably result from the high viscosities of the silica suspensions. The specificity for the formation of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is not influenced by the grafting of the catalyst for ligand/Cu=4. This silica-grafted Cu(II)-PS-Im demonstrates a stable conversion under suitable conditions for at least 150 hours in the oxidative coupling of 2,6-di-tert-butylphenol (DTBP) in a continuous stirred tank reactor.

5.1 Introduction

In order to combine the advantages of both homogeneous and heterogeneous catalysts, we have developed a number of immobilized polymer-bound catalysts, e.g. silica-quaternized or adsorbed Cu(II)-PS-Im (Fig.1, type c) for oxidative coupling of 2,6-disubstituted phenols (Scheme 1) in toluene/methanol (13/2 v/v) [1]. Compared with immobilized polymer-bound pyridine-based [2,3] or 4-dimethylaminopyridine (DMAP) -based [4] copper(II) complexes, these imidazole-containing catalysts showed intermediate catalytic activity, but better specificity for the formation of PPO. Moreover, under suitable conditions they proved to be stable catalysts in a continuous phenol-oxidation process [1].



Scheme 1

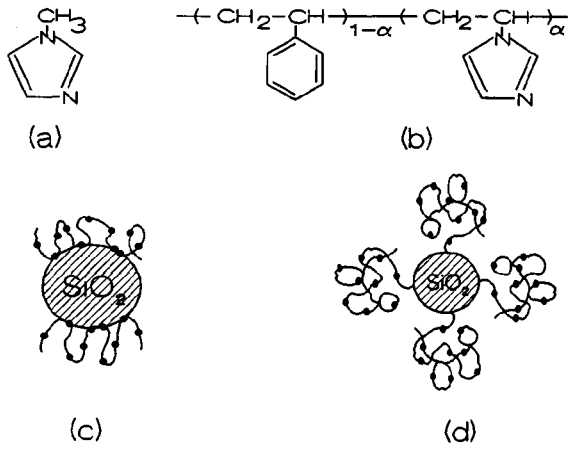


Fig.1 Schematic representation of free and immobilized imidazole ligands in Cu(II) complexes as catalysts: (a) NMIm; (b) PS-Im; (c) silica-quaternized or adsorbed PS-Im; (d) silica-grafted PS-Im.

In previous studies we have already investigated non-immobilized copper(II) complexes of N-methylimidazole (Cu(II)-NMIm) [5] and Cu(II)-PS-Im [6] as catalysts (Fig.1, types a and b) for the oxidative coupling of DMP. In both cases mononuclear $[Cu(imidazole)_4]^{2+}$ species at high ligand/Cu ratios were found to be the better catalyst precursors and more favourable for PPO formation than dinuclear complexes. In addition, toluene/methanol (13/2 v/v) appeared to be a suitable solvent mixture for obtaining both high activity and

good specificity.

In general, immobilization of polymeric catalysts by graft copolymerization is a method yielding more effective catalysts than other methods, e.g. adsorption of polymer chains on silica. Therefore, in the present study the preparation and catalysis of silica-grafted Cu(II)-PS-Im (Fig.1, type d) will be described. Besides, some similarities as well as differences in their catalytic behaviour in a batch-type reactor will be pointed out in comparison with silica-quaternized, or adsorbed Cu(II)-PS-Im, as well as non-immobilized Cu(II)-NMIm or Cu(II)-PS-Im catalytic systems. Finally, application of silica-grafted Cu(II)-PS-Im as catalyst for oxidative coupling of DTBP in a continuous reaction process will be reported.

5.2 Experimental

5.2.1 Materials.

$CuCl_2(H_2O)_2$ (analytically pure), KOH and methanol (Uvasol) (Merck) were used as received. N-vinylimidazole (NVIm) and styrene (Aldrich) were distilled from KOH under reduced N_2 atmosphere. DMP (Aldrich) was purified by repeated recrystallization from n-hexane. DTBP (Janssen) was used without further purification. Toluene (Merck) was dried over Na. The non-porous Aerosil 200V (specific surface $\simeq$200 $m^2.g^{-1}$, average sphere diameter 12 nm) containing $\simeq$1.0 mmol "-SiOH" per gram silica was kindly provided by Degussa AG. Hexamethyldisilazane (HMDS) (Janssen) was used as supplied.

5.2.2 Non-immobilized PS-Im

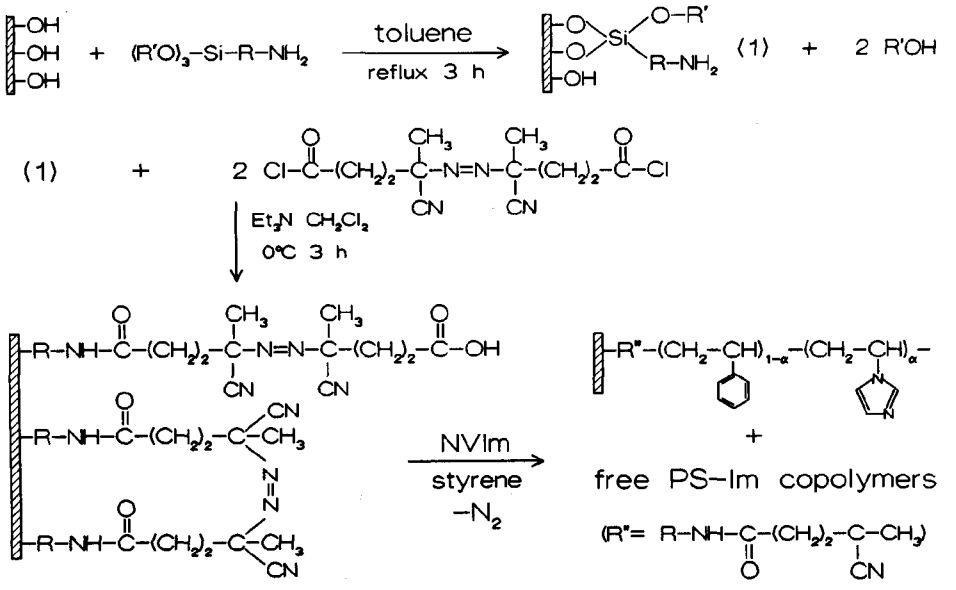
Radical copolymerization of NVIm and styrene was performed in toluene using AIBN as an initiator. This copolymerization and the characterization of non-immobilized PS-Im were carried out as reported previously [6].

5.2.3 Aerosil 200V-grafted PS-Im

Scheme 2 outlines the preparation of silica-bound initiator and subsequent radical graft copolymerization of NVIm and styrene on Aerosil 200V.

The silica-bound 4,4'-azo-bis(4-cyanopentanoic acid) was prepared according to a literature procedure [7]. The sample applied in the present case contained 0.14 mmol of "-N=N-" per gram silica (calculated from elemental analysis: C, 5.01; H, 0.71; N, 1.18; Aerosil, 92.0). On the average, 0.28 mmol of "-SiOH" and 0.22 mmol "-NH_2" per gram silica remained on the surface of silica spheres (calculated from elemental analysis: C, 4.13; H, 0.48; N, 0.47;

Aerosil, 94.5).



Scheme 2

For graft copolymerizations 1.0 gram of silica-bound initiator was suspended in 12 ml toluene under N_2 atmosphere at room temperature. Stoichiometric amounts of monomers were added to the suspension, which was then stirred at 70 °C for 6-24 hours. Subsequently, this reaction mixture was centrifuged (decanting the upper layer) and suspended in another 120 ml toluene/methanol (13/2 v/v) and stirred for at least 3 hours. This procedure was repeated three times in order to remove the free copolymers. Then, the loaded silica particles were again suspended in 30 ml toluene and slowly poured into a fifteen fold volume of petroleum ether 40-60, filtered, dried in high vacuum at 60 °C for 3 days and characterized by elemental analysis. The free copolymers were precipitated from the supernatant in petroleum/ether (2/1 v/v) and re-precipitated twice from chloroform, then dried and characterized as above. All results of preparation and characterization of Aerosil 200V-grafted PS-Im are compiled in Table I.

For sample G in Table I, the silica surface of the initiator was made hydrophobic with HMDS before the graft copolymerization was started. Trimethyl

silylation of the free silanol groups on silica was performed by suspending the silica-bound initiator (2.0 grams) in 30 ml toluene over P_2O_5 under dry N_2 atmosphere and subsequently adding HMDS. Then, this suspension was stirred at 20 °C for 14 hours. Such procedure was known to be successful for capping of free silanol groups [8] and did not give rise to destruction of siloxane bonds by formed NH_3 as found by Buszewski [9] at 110°C in the absence of P_2O_5. The material was separated from solution by centrifuging, washed twice with dichloromethane and dried in high vacuum at 20 °C overnight.

Table 1 Graft Copolymerizations of NVIm and Styrene on Aerosil 200V[a]

Samples	%Mole of NVIm	Time (h)	α^b (%)	θ^c (%)	Conversion (Wt.%) graft	free	total
A	34	6	6.2	23	2.6	2.4	5.0
B	52	6	12	26	3.1	4.1	7.2
C	52	12	12	30	4.2	6.4	11
D	52	24	12	32	4.3	8.6	13
E	62	6	17	27	3.0	3.1	6.1
F	71	6	23	18	1.7	2.6	4.3
G[d]	52	17	10	16	1.3	3.5	4.8

[a]Reactions were carried out under N_2 at 70°C; amount of Aerosil 200V-bound initiator based on total monomers is 0.12 mol% of "-N=N-" groups; toluene/monomers=1/1 (v/v).

[b]Chain loading of PS-Im with imidazole groups.

[c]Loading degree: wt.% of PS-Im on Aerosil 200V.

[d]Silica surface of initiator was modified with hydrophobic "-Si(CH_3)$_3$" groups.

5.2.4 VIS and EPR measurements

VIS spectra of Aerosil 200V-grafted Cu(II)-PS-Im in solution were recorded on a PERKIN-ELMER Lambda 2 UV/VIS Spectrophotometer at room temperature (stirring the suspension during measurement). EPR spectra of frozen solution of Aerosil 200V-grafted Cu(II)-PS-Im were recorded on a JES-RE 2X EPR Spectrometer at -196°C.

5.2.5 Oxidative coupling in a batch-type reactor

The oxidative coupling polymerization of DMP was carried out in a round flask with stirring, instead of shaking of the cylindrical reaction vessel [6], to prevent loaded silica particles from sticking on the top wall of the vessel. Immobilized polymeric catalysts were prepared in situ by suspending the Aerosil 200V-grafted PS-Im in toluene and adding $CuCl_2$/methanol solution. The coordination equilibrium period lasted about 24 hours. After saturating the reaction system with O_2, the reactions were started by adding hydroxide (as KOH dissolved in methanol) and DMP, subsequently. Steady state reaction rates R were obtained by measuring O_2 uptake as a function of time with an automatic isobaric gas burette. Relative observed reaction rates (k_{obs}) for a definite substrate concentration were calculated as $k_{obs} \equiv R/[CuCl_2]_0$ assuming that all $CuCl_2$ yields active catalyst. The stirring speed of the reaction solution was sufficient to prevent gas-liquid diffusion of O_2 becoming rate determining. The following standard conditions were applied: T= 25 ^{o}C; Po_2= 101.3 kPa; [DMP]= 0.06 mol.dm^{-3}; and [Cu(II)]= 0.33x[OH^-]= 0.25x[imidazole]= 0.83 mmol.dm^{-3}; solvent mixture, toluene/methanol (13/2 v/v); total reaction volume, 0.015 dm^3.

5.2.6 Continuous oxidative coupling process

Fig.2 shows the set-up for continuous oxidative coupling. The diameter of pores in the applied polytetrafluoroethylene membrane is 20 nm. However, the grafted polymer chains bound to silica prevent the loaded silica particles from passing through the membrane [4]. Moreover, leaching of Cu(II) from the polydentate coils as well as detachment of grafted polymeric ligands from silica appeared to be negligible [4]. The standard conditions were: T= 25 ^{o}C; Po_2= 101.3 kPa; $[DTBP]_0$= [DTBP]= 0.02 mol.dm^{-3}; and $[Cu(II)]_0$= 0.67$[OH^-]_0$= 0.25x$[imidazole]_0$= 0.21 mmol.dm^{-3}; solvent mixture, toluene/methanol (13/2 v/v); total reaction volume, 0.15 dm^3; flow rate, 0.2 cm^3.min^{-1}. The coordination equilibrium period lasted about 24 hours and followed by an addition of hydroxide (as KOH dissolved in methanol).

5.2.7 Determination of DPQ

In batch-type experiments, once the reaction was complete the reaction mixture was immediately diluted with chloroform and subsequently the overall catalytic specificity was determined by measuring the concentrations of the side product 3,5,3',5'-tetramethyl-4,4'-diphenoquinone (DPQ) with a PYE Unicam SP-8-200 UV/VIS Spectrophotometer at 421 nm (ε=74,000 dm^3.mol^{-1}.cm^{-1}) because

PPO and DPQ are practically the sole products from DMP.

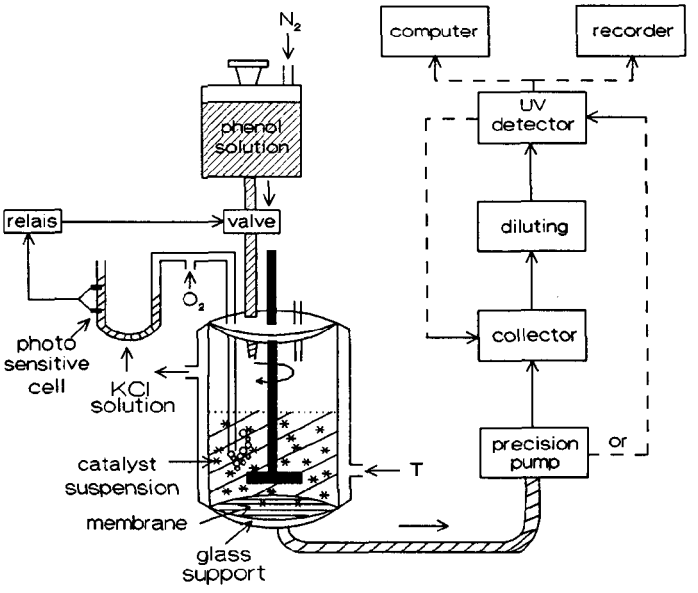


Fig.2 Schematic drawing of the apparatus for the continuous oxidative coupling process of phenols catalyzed by silica-grafted Cu(II)-PS-Im.

For continuous experiments, DTBP was used as a substrate since it yields only one main product, viz. its DPQ (Scheme 1), which could be detected by UV/VIS spectrophotometry at 426 nm (ε=65,000 $dm^3.mol^{-1}.cm^{-1}$) after strong dilution with chloroform. From these data the stability of the catalyst could be derived.

5.3 Results and Discussion

5.3.1 Graft copolymerization

The preparation and the type of initiator bound to Aerosil 200V (Scheme 2) are different from those reported by Verlaan et al. [2] and Koning et al. [4]. On the average, 28% of free "-SiOH" remained on the silica surface instead of 40% of free "-SiOH' in Koning's case; this lower value seems to be more favourable for high catalytic activity.

In order to obtain silica-grafted PS-Im having a reliable and narrow range of chain loading (α) with imidazole groups, the final conversions of graft copolymerizations were kept below 15%. Because of the similar α values of both silica-grafted and free copolymers [4], we took the α values in Table I from free PS-Im by elemental analysis and applied them to the immobilized copolymers. By using the Fineman and Ross method, the reactivity ratios of monomers were calculated to be r_1=0.07 and r_2=7.0 for NVIm and styrene, respectively. The same values were also obtained for non-grafted copolymerization initiated by AIBN [6].

Finally, very long times of graft copolymerization (>12 hours) seem not to yield higher loading degrees (θ) of PS-Im on silica, but produced more free copolymer in solution (Table I samples B-D), as was also found for graft polymerizations of methyl(methacrylate) and explained in terms of radical recombination on silica surface and the Trommsdorff effect in the surrounding medium [7].

5.3.2 Catalysis in a batch-type reactor

As found in the cases of non-immobilized Cu(II)-NMIm [5] and Cu(II)-PS-Im [6], no reaction takes place in the absence of base with immobilized polymeric catalyst (Table II). However, in the present case a maximum in catalytic activity is found for silica-grafted Cu(II)-PS-Im around OH/Cu=3 instead of OH/Cu= 1 and 2 for Cu(II)-NMIm [5] and Cu(II)-PS-Im [6], respectively. Apparently, on immobilizing Cu(II)-PS-Im on silica, its stability against base improves. The main role of hydroxide is to produce the reactive phenolate anions from DMP [10,11], whereas an excess of base somehow induces catalyst destruction by forming copper hydroxides [1,5,6]. A control experiment proved that detachment of grafted polymeric ligands by base from silica does not take place under standard conditions even in the absence of neutralizing DMP.

Table 2 Effect of OH/Cu on catalysis under standard conditions

catalyst	OH/Cu	$k_{obs} x10^3$ (s^{-1})	DPQ (%)
Aerosil 200V-	0	0	-
grafted	1	1.2	12
Cu(II)-PS-Im	2	2.3	12
(sample B)	3	6.5	12
	4	3.2	-

In previous studies with non-immobilized catalytic systems, we found higher reaction rates for higher ligand/Cu ratios, because of the apparent formation of more mononuclear $[Cu(imidazole)_4]^{2+}$. Enhancement of reaction rates was obtained even for ligand/Cu>30 in case of Cu(II)-NMIm [5], but only up to 10 for Cu(II)-PS-Im due to the overlap of polymer coils in concentrated solution [6]. However, with silica-grafted Cu(II)-PS-Im as catalyst, high ligand/Cu ratios require a large number of loaded silica particles. Then, the high viscosity of the silica suspension probably limits diffusion of reactants. Consequently, no increase in reaction rate is observed for ligand/Cu>4 (Table III).

For silica-grafted Cu(II)-PS-Im as catalyst, the % DPQ of about 12% is independent of the applied OH/Cu and ligand/Cu ratios (Tables II & III). This differs from the cases of Cu(II)-NMIm [5] and Cu(II)-PS-Im [6], for which increasing ligand/Cu ratios are always accompanied by a decrease in % DPQ down to 6%, resulting from the transformation of dinuclear complexes into more specific mononuclear species.

Table 3 Effect of ligand/Cu on catalysis under standard conditions

catalyst	ligand/Cu	$k_{obs} x10^3$ (s^{-1})	DPQ (%)
Aerosil 200V-	0	0	-
grafted	1	0.56	11
Cu(II)-PS-Im	2	4.4	12
(sample B)	4	6.5	12
	10	5.4	14
	22	1.1	-

We also investigated the kinetics of oxidative coupling polymerization of DMP catalyzed by Aerosil 200V-grafted Cu(II)-PS-Im as a function of substrate concentration. Under standard conditions so-called saturation kinetics are observed and the double-reciprocal Lineweaver-Burk plot of reaction rate versus DMP concentration is given in Fig.3. A straight line intersects the Y axis in agreement with the well-known equation:

$$\frac{1}{R} = \frac{1}{k_2[E]_0} + \frac{K_m}{k_2[E]_0[DMP]}$$

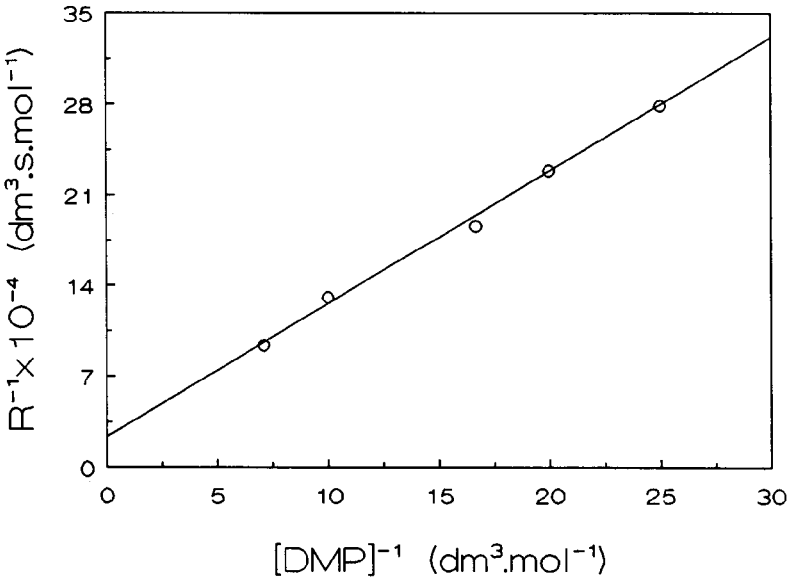
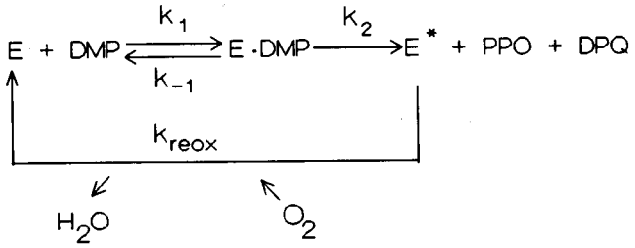


Fig.3 Double reciprocal Lineweaver-Burk plot of steady state reaction rate versus substrate concentration under standard conditions for Aerosil 200V-grafted Cu(II)-PS-Im (sample B) as catalyst.

Therefore, this reaction can be described by a Michaelis-Menten mechanism as given in Scheme 3.



Scheme 3

E is the active Cu(II)-PS-Im complex; E^* is the Cu(I) complex; $[E]_0$ is overall concentration of the active Cu(II) ions; k_2, rate constant of rate-determining step; $K_m=(k_{-1}+k_2)/k_1$, the Michaelis-Menten constant. From the straight line in

Fig.3, k_2 and K_m^{-1} (K_m^{-1} is a measure of the accessibility of active site for substrate) have been calculated yielding k_2=0.052 s^{-1} and K_m^{-1}=2.3 $dm^3.mol^{-1}$. These values imply that the reduction in reaction rate, after grafting, as compared to that for non-immobilized Cu(II)-PS-Im with k_2=0.15 s^{-1} and K_m^{-1}=1.7 $dm^3.mol^{-1}$, is caused either by a decrease of the intrinsic activity of catalytic sites (k_2), or by a decrease of $[E]_0$ ($[E]_0<[CuCl_2]_0$) due to incomplete complexation of $CuCl_2$. Fortunately, the latter possibility could be excluded by the following result. After centrifuging the silica-grafted Cu(II)-PS-Im from solution (standard conditions except addition of DMP), Cu(II) ions were found by atomic absorption to be less than 10^{-2} ppm in aliquots of the supernatant solution. This result proves that less than at most 0.025% of Cu(II) ions is present outside grafted PS-Im coils, i.e. $[E]_0=[CuCl_2]_0$. So, the reduction in reaction rate is only related to the decreased k_2.

5.3.3 Explanation of the reduced activity after grafting

Table IV demonstrates that grafting of PS-Im on silica does not affect the catalytic specificity (% DPQ) of its Cu(II) complexes. However, the relative observed reaction rates (k_{obs}) for silica-grafted Cu(II)-PS-Im are three times lower than those for non-immobilized Cu(II)-NMIm and Cu(II)-PS-Im. Several possible explanations will be considered taking into account that the reduction in reaction rate can be completely attributed to lowering of k_2.

First, water enrichment, owing to free hydrophilic silanol groups on the silica surface, might retard the catalytic process [12]. However, this interpretation is not supported by the experimental result for sample G having less free silanol groups (Tables I & IV). In fact, no enhancement in reaction rate is observed by using sample G for catalysis. Another effect of the free silanol groups could be adsorption of some imidazole ligands of PS-Im on silica, resulting in a decrease of the effective ligand/Cu ratio. The shortage of available imidazole ligands is unfavourable for the complete formation of the mononuclear $[Cu(imidazole)_4]^{2+}$ species [5,6], which might cause a decreased k_2. However, this possibility is not in agreement with the experimental result for sample G in Tables I & IV either. On the contrary, the basic "$-NH_2$" groups (0.22 mmol) left on the silica surface would prevent the interaction between silanol and imidazole groups.

By using sample B in Table I as an example, the available area for a polymer chain on silica surface was calculated to have a radius of 37.3 Å ($\bar{M}_n$ of grafted PS-Im assumed to be the same as that of free copolymer, viz. 46,000

$g.mol^{-1}$). On the other hand, in terms of Flory's statistical theory ($R_g^2=\langle r^2\rangle/6$ and $\langle r^2\rangle=C_\infty nl^2$ assuming a θ state), we calculated the radius of gyration of free PS-Im yielding R_g=68.3 Å by taking C_∞=10 and l=2.5 Å. Apparently, the values of 37.3 and 68.3 Å imply that some overlap of polymer coils on the surface of silica spheres should take place, which may affect the structure of the Cu(II) complexes.

The VIS spectrum of silica-grafted Cu(II)-PS-Im in solution (sample D, standard conditions except addition of DMP) showed a broad absorption of the Cu(II) complex in the range of 600-850 nm, which might indicate the presence of both mono- and dinuclear Cu(II) complexes [5]. In addition, Fig.4 (a) presents an EPR spectrum of a frozen solution of silica-grafted Cu(II)-PS-Im (ligand/Cu=4). Obviously, the optimum mononuclear species $[Cu(imidazole)_4]^{2+}$

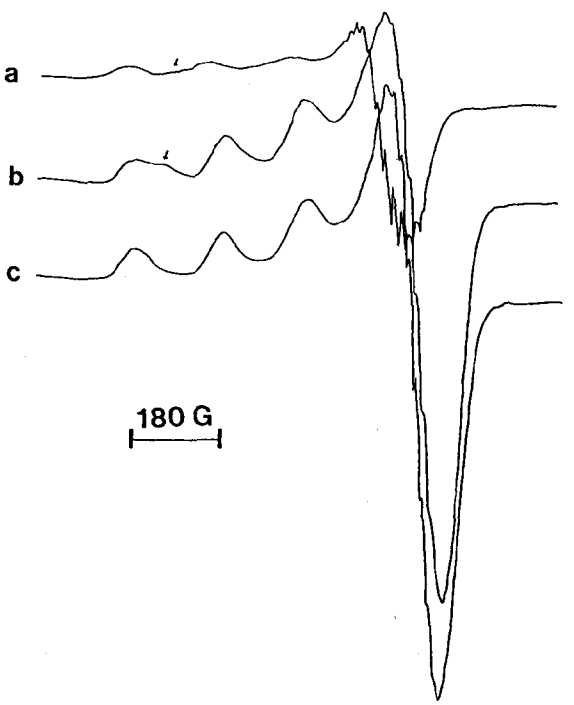


Fig.4 EPR spectra of frozen solution of (a) Aerosil 200V-grafted Cu(II)-PS-Im (sample D), standard conditions except addition of DMP, receiver gain, $2x10^2$; (b) Cu(II)-PS-Im with ligand/Cu=2 (ref.6); (c) Cu(II)-PS-Im with ligand/Cu=4 (ref.6).

($g_{\perp}$=2.04, $g_{//}$=2.24, $A_{//}$=179 G and A_N=15.1 G) is present [6,13]. Unfortunately, the turbid sample of Cu(II)-PS-Im grafted on silica can not give clear signals of possible other Cu(II) species in its EPR spectrum.

The EPR spectrum of grafted Cu(II)-PS-Im at position (↓) (Fig.4, a) looks similar to that of non-immobilized Cu(II)-PS-Im with ligand/Cu=2 (Fig.4, b) rather than to that with ligand/Cu=4 (Fig.4, c). In cases of non-immobilized Cu(II)-PS-Im with ligand/Cu=2, we have already reported the coexistence of $[Cu(imidazole)_4]^{2+}$ and $[Cu(imidazole)_{1-3}]^{2+}$ species, thus yielding half of the optimum reaction rate [6]. Therefore, in the present case of silica-grafted Cu(II)-PS-Im under standard conditions with ligand/Cu=4, the decrease in reaction rate after grafting is primarily attributed to the incomplete transformation of Cu(II) ions into the optimum complex $[Cu(imidazole)_4]^{2+}$, probably owing to overlap of polymer coils on silica surface (see above) and partial aggregation of imidazole groups. In other words, steric hindrance of overlapping polymer chains on the silica surface and non-uniform distribution of imidazole ligands are unfavourable for the complete formation of the symmetrically planar $[Cu(imidazole)_4]^{2+}$ complex. The presence of $[Cu(imidazole)_{1-3}]^{2+}$ species will result in rather low intrinsic activities of catalytic sites (k_2).

We have already tried to promote the transformation of $[Cu(imidazole)_{1-3}]^{2+}$ species into the optimum complex by adding extra low molar mass imidazole ligands, viz. NMIm with NMIm/Cu=2-4. However, in the presence of extra NMIm a decreased reaction rate was observed under standard conditions with OH/Cu=3. This seems to indicate that the extra-added NMIm ligands extract some Cu(II) ions from silica-grafted polymer coils to form some low molar mass complexes, rather than promote the formation of $[Cu(imidazole)_4]^{2+}$ species. The Cu(II)-NMIm complex is known to be unstable at OH/Cu=3 [5].

It seems from the above discussion that lowering the loading degree (θ) of PS-Im on silica might prevent overlap of polymer coils on silica surface, thus permitting a higher activity of the catalyst. Unfortunately, no enhancement in reaction rate was found by applying the sample G as catalyst having a value of θ=16% (Tables I & IV) instead of 26% for sample B. In fact, for a value of only θ=13% the radius of the available area for a polymer chain on silica surface would be $\sqrt{2}$x37.3=52.2 Å (referring to sample B in Table I, for which 37.3 Å was calculated), which is still smaller than the value of R_g=68.3 Å. Therefore, overlap of polymer coils on silica surface may still occur for sample G. Rather low loading degrees (θ) of PS-Im on silica, e.g.

θ<6.5% in the present case, are required to prevent overlap of grafted polymer coils. However, this would involve a four fold increase of the number of the loaded silica particles for constant ligand/Cu ratio. Then, the high viscosity of the silica suspension and possible interparticle complexation would limit the diffusion of reactants. So, increasing reaction rates would not be observed either.

5.3.4 α effect on catalytic activity

As shown in Fig.5, a maximum reaction rate is observed at α=12% with non-immobilized Cu(II)-PS-Im. This effect of chain loading (α) of PS-Im with imidazole groups on catalytic activity was discussed in a previous paper [6] in terms of strain in the polymer chain segments between neighbouring ligands [14,15]. However, after grafting of PS-Im on silica, this effect nearly disappears (Fig.5). In section 5.3.3, the overlap of polymer chains on silica surface and the aggregation of some imidazole ligands were described. In this case, the Cu(II) ions may be coordinated by imidazole ligands from different

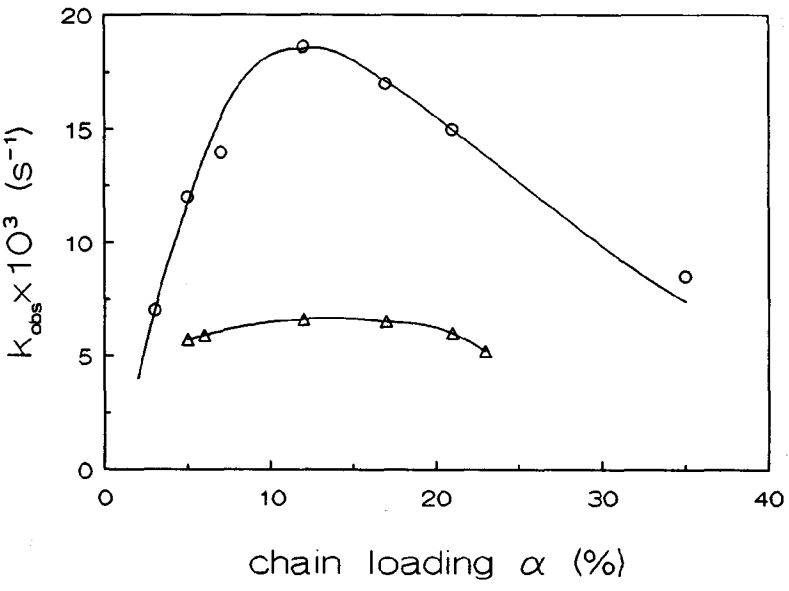


Fig.5 Effect of chain loading (α) on reaction rate under standard conditions: (o) for non-immobilized Cu(II)-PS-Im and [Cu(II)]= [OH^-]= 0.25x[imidazole]= 3.32 mmol.dm^{-3}; (Δ) for Aerosil 200V-grafted Cu(II)-PS-Im.

polymer chains. Then, strain in the polymer chain segments between neighboring ligands will hardly change with increasing α. This is different from the case of isolated free polymer coils, wherein the Cu(II) ions solely coordinate with imidazole ligands attached to the same polymer chain.

5.3.5 Comparison with other immobilized catalysts

It appears from Table IV that silica-grafted Cu(II)-PS-Im is

Table 4 Comparison for different catalytic systems under comparable conditions

catalysts	ligand/Cu	OH/Cu	$k_{obs} x10^3$ (s^{-1})	DPQ (%)
Cu(II)-NMIm	4	1	21	14
Cu(II)-PS-Im	4	1	19	15
Aerosil OX50-quaternized Cu(II)-PS-Im (α=12%; θ=5.9%)	4	3	4.0	10
Aerosil OX50-adsorbed Cu(II)-PS-Im (α=35%; θ=9.5%)	4	3	4.1	14
Aerosil 200V-grafted Cu(II)-PS-Im (sample C)	4	3	7.3	11
(sample D)	4	3	7.1	11
(sample G)	4	3	6.9	11
Aerosil 200V-grafted Cu(II)-PS-Py (α=25%; θ=38%)[a]	2	1	<1.0	>40[b]
Aerosil 200V-grafted Cu(II)-PS-DMAP (α=30%; θ=28%)[c]	4	1	16	19

[a] In 1,2-dichlorobenzene/methanol (ODCB/MeOH) (13/2 v/v) and for [DTBP]=0.18 mol.dm^{-3} (ref.3).

[b] For non-immobilized Cu(II)-PS-pyridine in ODCB/MeOH (13/2 v/v) (ref.17).

[c] In ODCB/MeOH (13/2 v/v) (ref.4).

catalytically more active than silica-quaternized or adsorbed Cu(II)-PS-Im. Grafted polymer chains are longer and more extended than the loops and tails of quaternized or adsorbed chains [16], which was considered to be favourable for catalytic activity [4].

Finally, the present grafted imidazole-containing catalysts show better catalytic specificity for PPO formation and intermediate catalytic activity compared with grafted pyridine or DMAP-based catalytic systems under proper conditions (Table IV). In view of the high basicity of the DMAP ligand, one can understand the higher activity of the DMAP-based catalytic system. Unfortunately, the strong basicity of DMAP prevents successful application of this DMAP-type catalyst in a continuous phenol-oxidation process [4].

5.3.6 Stability of catalysts

Aerosil 200V-grafted Cu(II)-PS-Im has been applied as catalyst for the oxidative coupling of DTBP in a continuous stirred tank reactor (CSTR) (Fig.2). Under standard conditions with $(OH/Cu)_0$=1.5, a stable DTBP conversion is observed for at least 150 hours (Fig.6). This result not only demonstrates

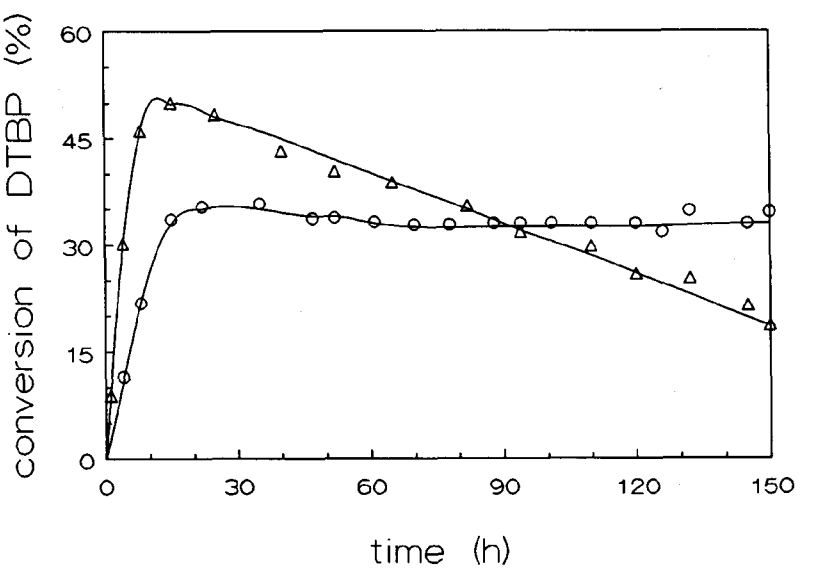


Fig.6 Stability of Aerosil 200V-grafted Cu(II)-PS-Im (sample F) as catalyst for oxidative coupling of DTBP in CSTR under standard conditions: (o) $(OH/Cu)_0$=1.5; (Δ) $(OH/Cu)_0$=3.

successful application of an immobilized polymeric catalyst in a continuous process, but also confirms that phenolate anions, produced from initial hydroxide and DTBP, are regenerated during the oxidative coupling and do not escape from the catalytic intermediate. This fact should be taken into account when considering the mechanism of oxidative coupling of phenols catalyzed via Cu(II)-amine complexes. However, the decreasing conversion in case of $(OH/Cu)_0$=3 as shown in Fig.6 indicates that higher initial base concentrations are not suitable anymore for a continuous catalytic process, probably because of gradual destruction of some base coordinated catalysts during a long period. Only in the initial stage the rate is enhanced for higher OH/Cu ratio as expected from the results in batch processes (see Table II)

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Chapter 6

Preparation of Telechelics by Oxidative Coupling Copolymerization of 2,6-Dimethylphenol with Tetramethyl Bisphenol-A Catalyzed by Copper(II) Complexes of N-methylimidazole

Abstract: A series of copolymerizations of 2,6-dimethylphenol (DMP) with 2,2-di(4-hydroxy-3,5-dimethylphenyl)propane (tetramethyl bisphenol-A, TMBPA) catalyzed by N-methylimidazole copper(II) complexes in toluene/methanol (12/3 v/v) was performed with TMBPA/Cu=1. The main product α,ω-bis(2,6-dimethylphenol)-poly(2,6-dimethyl-1,4-phenylene oxide) (PPO-2OH) was characterized by ^{1}H-NMR spectroscopy and GPC. It consisted of PPO-type telechelics carrying two hydroxyl end groups with $\bar{M}_n$ in the range of 3400-5000 g.mol^{-1} and $\bar{M}_w/\bar{M}_n$ ratios about 1.5. The formation of side products, i.e. homopolymer poly(2,6-dimethylphenylene oxide) (PPO) and 3,3'5,5'-tetramethyl-4,4'-diphenoquinone (DPQ), could be suppressed by slowly adding the DMP to the reaction system. A likely phenoxonium intermediate mechanism is derived from this copolymerization study.

6.1 Introduction

The synthesis of PPO-type telechelics with two hydroxyl end groups (PPO-2OH), a potential precursor for the preparation of block copolymers like polyesters [1,2], has been accomplished be means of White's method [3], electro-oxidative polymerization [4], electrophilic condensation reaction [5], pyridine-type copper(I) complexes as catalysts [5,6] and phase transfer catalyzed polymerization [7]. In general, a radical-radical mechanism or a radical-anion mechanism was presented to explain the formation of PPO-2OH, depending on the type of reaction system [3-7].

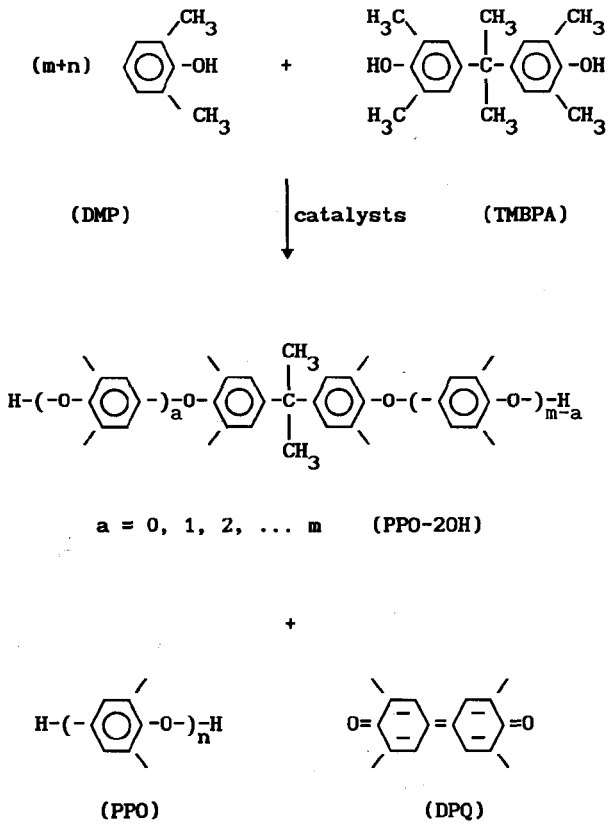
Recently, we systematically investigated the oxidative coupling polymerization of DMP catalyzed by imidazole-based copper(II) complexes [8-11] and proposed a possible mechanism via a phenoxonium intermediate [12].

The goal of this communication is to describe a synthetic procedure for the preparation of PPO-2OH based on oxidative coupling polymerization catalyzed by N-methylimidazole copper(II) complexes (Cu(II)-NMIm). It involves the copolymerization of DMP with small amounts of the bifunctional TMBPA (Scheme 1).

6.2 Experimental

6.2.1 Materials

$CuCl_2(H_2O)_2$ was obtained analytically pure from Merck. N-methylimidazole (NMIm) (Aldrich) was distilled from KOH under reduced N_2 pressure. DMP (Aldrich) was purified by repeated recrystallization from n-hexane. KOH, toluene (dried over Na) and methanol (Uvasol quality) were from Merck and used without further purification.



Scheme 1

6.2.2 Synthesis of TMBPA

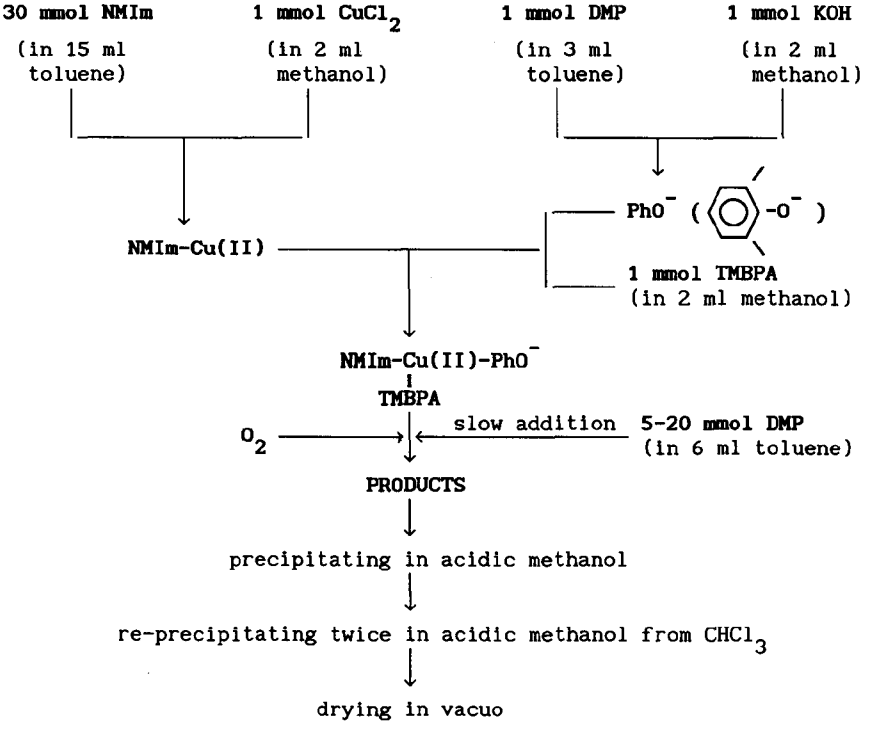
TMBPA was prepared in terms of a literature procedure [13]. The obtained white crystals were characterized by elemental analysis (calculated for $C_{19}H_{24}O_2$: C, 80.2; H, 8.5; found: C, 80.3; H, 8.6.) and ^{1}H-NMR: 1.60 (s, $-C(CH_3)_2-$, 6H); 2.21 (s, Ph-CH_3, 12H); 4.50 (s, Ph-OH, 2H); 6.84 (s, Ph-H, 4H).

6.2.3 Techniques

^{1}H-NMR spectra (300 MHz) were recorded on a Varian 300 NMR Spectrometer. GPC measurements were performed on a Waters 150-C ALC/GPC Instrument, using THF as solvent (1 ml/min, 32 ^{o}C). The eluent was monitored by refractive index and a calibration plot was constructed with polystyrene standards.

6.2.4 Preparation of PPO-2OH

Scheme 2 illustrates a procedure for the synthesis and isolation of PPO-2OH, which was derived from our mechanistic insights into the present oxidative coupling copolymerization of DMP with TMBPA. The copolymerization reactions were carried out in a three-necked flask, equipped with a septum stopper and a magnetic stirring bar, under O_2 atmosphere. DMP dissolved in toluene was slowly added to the reacting system by a perfusor syringe injector at a constant rate. The used standard conditions were: $CuCl_2$= PhO^-= TMBPA= 1 mmol; NMIm/Cu=30; solvent mixture, toluene/methanol (12/3 v/v); total reaction



Scheme 2 Schematic representation of preparation of PPO-2OH.

volume, 30 ml; addition rate of DMP/toluene solution, 0.16 ml/min; T=20 °C; Po_2=101.3 kPa.

6.2.5 Determination of DPQ

After stopping the reaction (the total reaction time is mentioned in Table 1), 1 ml of the reaction mixture was immediately diluted with chloroform and subsequently the concentration of DPQ was determined with a PYE Unicam SP-8-200 UV/VIS Spectrophotometer at 421 nm (ε=74,000 $dm^3.mol^{-1}.cm^{-1}$). From these data the percentage of reacted DMP that has been transformed into DPQ was calculated.

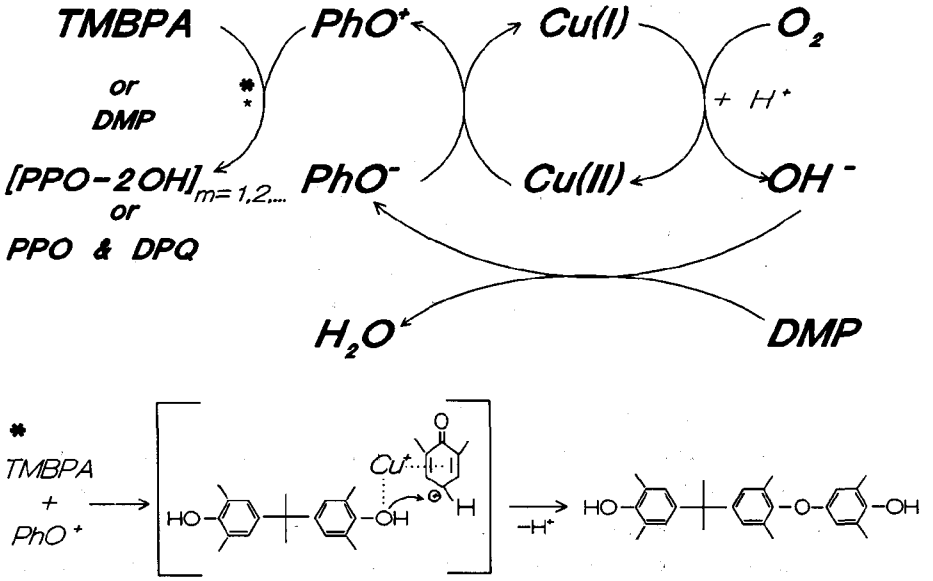
6.3 Results and Discussion

A possible mechanism for the copolymerization of DMP with TMBPA is briefly outlined in Scheme 3 (A). This is derived from the proposed mechanism of oxidative coupling polymerization of DMP in the absence of TMBPA [12,14].

In previous investigations using Cu(II)-NMIm complexes as catalysts, it was found that the base is the so-called co-catalyst producing phenolate anions from DMP, which appear to be essential for the start of the reaction [8]. So, one may expect that formation of phenolate anions by base is also the preliminary step in the copolymerization of DMP with TMBPA.

For the copolymerization of DMP with TMBPA under standard conditions, a large excess of TMBPA to Cu(II) ions, e.g. TMBPA/Cu=7.5, results in PPO-2OH with a very broad molecular weight distribution, i.e. a polydispersity index $D= \bar{M}_w/\bar{M}_n$ = 4-8, owing to the propagation of PPO chains starting from different TMBPA's. On the other hand, a ratio of TMBPA/Cu=0.5, i.e. the ratio of TMBPA-hydroxyl groups to Cu(II) ions equals 1, leads to PPO-2OH with D=2.25. In this case, one may assume that one TMBPA molecule can coordinate with two copper ions and PPO chains grow from both hydroxyl groups of each TMBPA molecule. Obviously, both extremes appear unfavourable for the formation of PPO-2OH with a narrow molecular weight distribution. Therefore, a small excess of TMBPA with respect to Cu(II) ions, i.e. TMBPA/Cu=1, was preferred for further experiments. Table 1 summarizes the results obtained for TMBPA/Cu=1 under standard conditions.

As shown in Scheme 3 (A) a side-on coordinated phenoxonium cation, as described by Uechi et al. for a p-benzoquinone copper complex [15], can competitively react either with a TMBPA molecule forming PPO-2OH, or with a DMP molecule yielding PPO and DPQ (Scheme 1), depending on which one (TMBPA or DMP) would be attached to the copper ion. In general, TMBPA is expected to



* PPO-2OH instead of TMBPA in following cycles

Scheme 3 (A) Reaction scheme in case of starting the reaction by adding initial base to DMP.

coordinate stronger with copper ion because of its somewhat stronger basicity than DMP. Therefore, the reaction of the DMP phenoxonium cation with TMBPA should be preferred and the main product of this copolymerization would be PPO-2OH.

Addition of all DMP at the beginning of the reaction does not affect the polydispersity index of obtained PPO-2OH, but only results in more DPQ (1.7%) as expected (exp.5 in Table 1). The corresponding PPO homopolymer can barely be detected in the ^{1}H-NMR spectrum of the telechelics (methanol-insoluble fraction) at δ=7.1 ppm (signal f in Fig.1: three aromatic protons in one PPO end group) [6].

By reducing the initial DMP concentration upon slow addition of DMP during the experiment, the amount of DPQ in the total product becomes only 0.5-0.6% (exp.1-4 in Table 1). Furthermore, one can no longer detect any PPO formation from the ^{1}H-NMR spectra (no signal at δ=7.1 ppm). A typical 300 MHz ^{1}H-NMR spectrum of PPO-2OH (Sample 4 in Table 1) is shown in Fig.2. The assignments are printed on the figure.

Table 1 Copolymerizations of DMP with TMBPA under standard conditions

exp. No.	DMP / TMBPA	addition time of DMP (min)	additional reaction time (min)	tele-chelics yield (%) a)	$\bar{M}_n$ (GPC)	D (GPC)	$\bar{M}_n$ (NMR) b)	DPQ (%)
1	5	40	20	25	3950	1.41	3600	0.6
2	10	40	20	43	3600	1.66	3400	0.5
3	20	40	20	77	3750	1.56	4100	0.6
4	10	40	60	60	4300	1.36	5000	0.5
5	20	0 c)	60	44	4200	1.42	3900	1.7

a) Wt.% of telechelics as methanol-insoluble fraction.

b) Calculation method taken from reference [6].

c) adding all DMP at the beginning of the reaction.

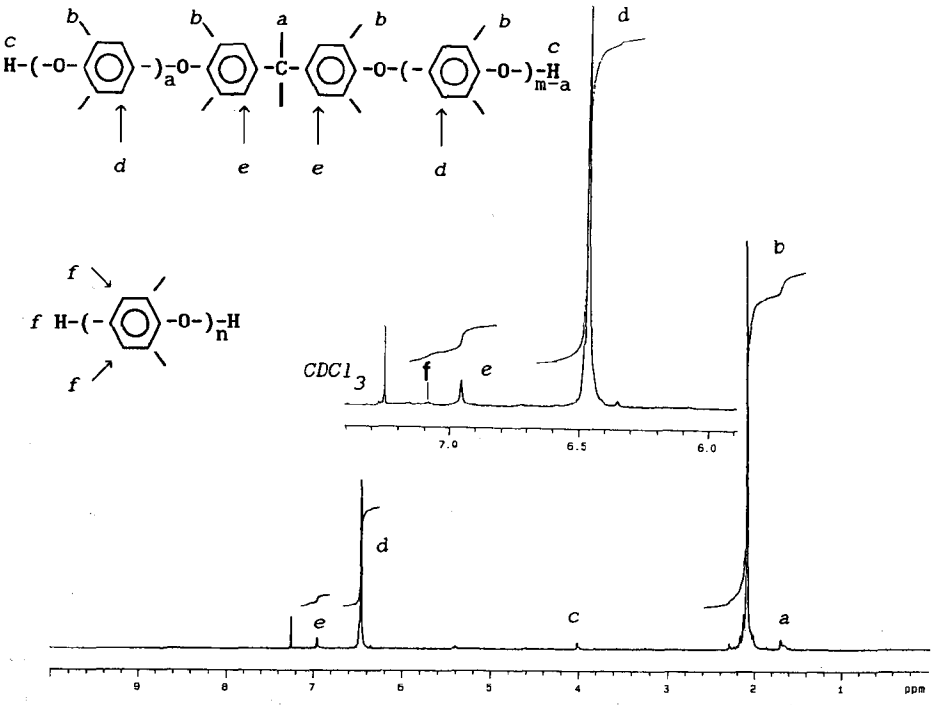


Fig.1 300 MHz ^{1}H-NMR spectrum of telechelics (sample 5 in Table 1); above is a expansion of the aromatic region of this spectrum, (in $CDCl_3$).

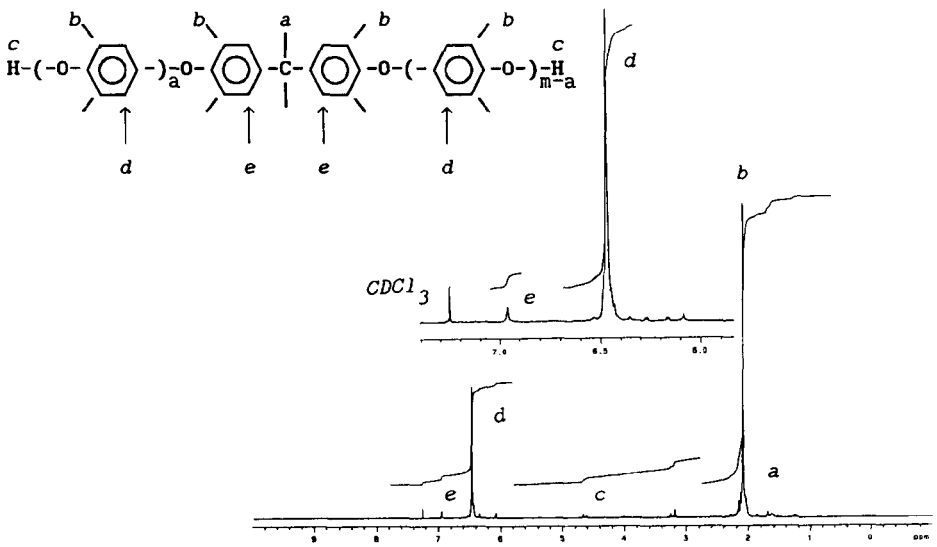


Fig.2 300 MHz ^{1}H-NMR spectrum of telechelics (sample 4 in Table 1);above is a expansion of the aromatic region of this spectrum, (in $CDCl_3$).

In addition, Fig.1 and 2 show no signal at δ=6.87 ppm, which would be expected for TMBPA segments remaining at the ends of PPO-2OH chains, i.e. in case of a=0 in Scheme 1 [5-7]. On the contrary, the signal e at δ=6.97 ppm in Fig.1 and 2 corresponds to TMBPA segments within the PPO-2OH chains [5-7]. So, by the present procedure only PPO-2OH are obtained that has grown starting from both sides of TMBPA units.

The yields of telechelics in Table 1 are the weight percentages obtained as methanol-insoluble fraction and increase with increasing total amount of added DMP (exp.1-3 in Table 1). Addition of more DMP might increase the average molecular weight of total PPO-2OH. Therefore, a larger amount of PPO-2OH will precipitate in acidic methanol from the reaction solution, resulting in higher yields.

$\bar{M}_n$ values in the range of 3400-5000 g.mol^{-1} and D= 1.36-1.66 for methanol-insoluble PPO-2OH are compiled in Table 1. They were derived from GPC measurements and ^{1}H-NMR spectra. By taking a 40 minutes longer additional reaction time (exp.4 versus exp.2 in Table 1), the yield increases from 43% to 60% and $\bar{M}_n$ increases from 3600/3400 g.mol^{-1} to 4300/5000 g.mol^{-1} (GPC/NMR). Taking account of the fact that no more dioxygen consumption takes place after

20 minutes additional reaction time, one must assume that some other kind of reaction is taking place at the later stage of the copolymerization in exp.4. This is most likely the so-called "re-distribution" between two PPO-2OH chains through a quinone ketal intermediate as proposed by Cooper et al. [16] and Mijs et al. [17], yielding more PPO-2OH with higher $\bar{M}_n$, which precipitate in an acidic methanol medium after the reaction. Fig.3 shows the GPC traces of these PPO-2OH obtained after shorter and longer additional reaction time (curve A: sample 2 and curve B: sample 4 in Table 1, respectively). The tail in curve A, representing a rather small amount of telechelics with low $\bar{M}_n$, disappears when taking longer additional reaction time (curve B). Therefore, a smaller D value of 1.36 was observed for sample 4 in Table 1.

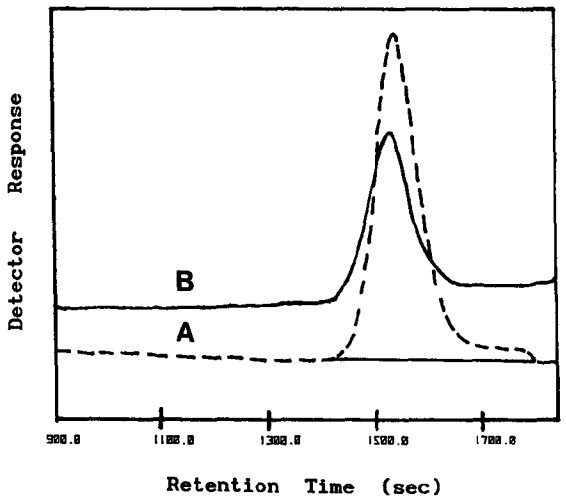
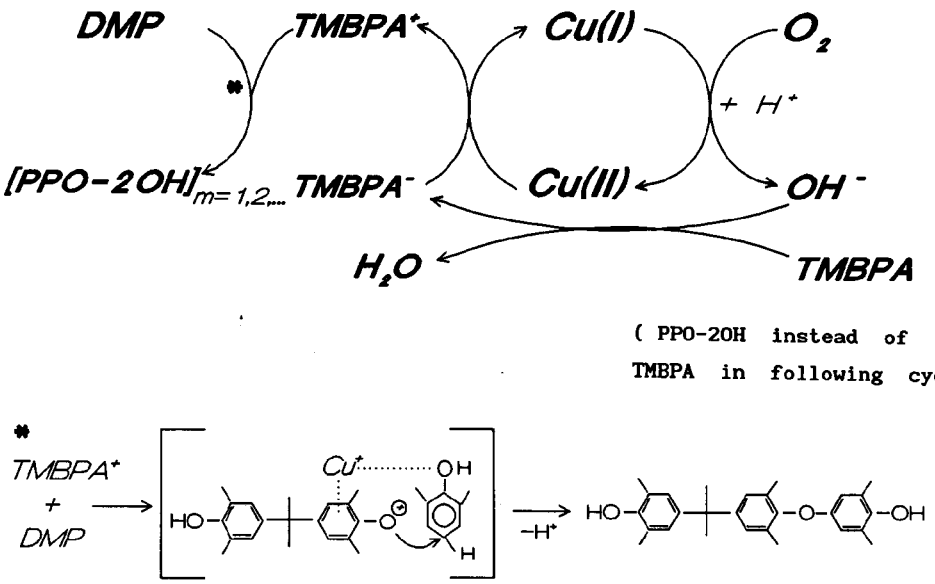


Fig.3 GPC traces of telechelics: (A) sample 2 in Table 1; and (B) sample 4 in Table 1.

In additional small-scale control experiments ([$CuCl_2$]= [KOH]= 3.32 mmol $.dm^{-3}$; NMIm/Cu=30; TMBPA/Cu=1; DMP/TMBPA=10; procedures taken as described previously for the oxidative coupling of DMP in a cylindrical reaction vessel with shaking [8,9]), a 40% higher reaction rate was observed by adding initial base to TMBPA instead of to DMP. This implies that once the TMBPA molecule is transformed into its phenolate anion, this TMBPA phenolate anion ($TMBPA^-$) appears to be a stronger coordinating ligand for the bridge between two copper ions [12]. Furthermore, due to the electro-donating isopropylidene group it

can be more readily oxidized to TMBPA phenoxonium cation ($TMBPA^+$). In this case, a partial positive charge may remain on one oxygen atom at the head position of TMBPA [18] and this may attack the para position of a DMP molecule through electrophilic substitution, yielding finally PPO-2OH. Such a pathway is outlined in Scheme 3 (B). Obviously, if the growth of PPO chains only starts from the head-oxygen position as mentioned above, DPQ should not be formed, However, 1.4% of DPQ was still found in the control experiment by adding the initial base to TMBPA and all DMP at the beginning of the reaction (like in exp.5 in Table 1). Therefore, in this case pathway (A) in Scheme 3 seems still to be responsible for the formation of small amounts of DPQ or PPO and some PPO-2OH, probably through a preliminary exchange reaction of $TMBPA^-$ with the excess DMP yielding some DMP^-, due to stronger acidity of DMP than TMBPA.

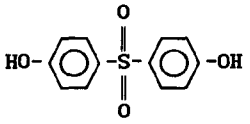


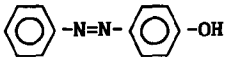
Scheme 3 (B) Reaction scheme in case of starting the reaction by adding initial base to TMBPA.

Accordingly, a combination of pathways seems to apply to this copolymerization: during the first oxidation cycle through pathway (A) in Scheme 3, then followed by pathway (B) in Scheme 3.

Finally, attempts to copolymerize DMP with 4,4'-sulfonyldiphenol (I) or

4-phenylazophenol (II) have been undertaken (procedures taken as in Scheme 2).





(I) (II)

Instead of copolymers only the DMP homopolymerization product PPO was obtained with a very low yield (less than 10%). This was confirmed by the ^{1}H-NMR spectra of products obtained as methanol-insoluble fractions. It is conceivable that the presence of the electro attracting sulfonyl or azo group in (I) or (II) prevents copolymerization because of the stronger acidity and higher oxidation potential of (I) and (II) with respect to DMP.

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Chapter 7

A Possible Mechanism of Oxidative Coupling Polymerization of 2,6-Dimethylphenol Catalyzed by Imidazole-Based Copper(II) Complexes

Abstract: Oxidative coupling polymerization of 2,6-dimethylphenol (DMP) catalyzed by copper-amine complexes is an important industrial process. Immobilization of homogeneous catalysts continues to receive increasing attention because of possible application in continuous processes. Therefore, both non-immobilized and immobilized imidazole-based copper(II) complexes have been investigated as catalysts for the oxidative coupling of DMP in a batch-type and continuous process, respectively. The present paper summarizes our experimental results and describes a possible mechanism, via a phenoxonium intermediate, of oxidative coupling of DMP catalyzed by imidazole-based copper(II) complexes.

7.1 Introduction

We have systematically investigated the oxidative coupling polymerization of DMP catalyzed by copper(II) complexes of N-methylimidazole (Cu(II)-NMIm) [1] or poly(styrene-co-N-vinylimidazole) (Cu(II)-PS-Im) [2] in toluene/methanol (13/2 v/v). In order to combine the advantages of both homogeneous and heterogeneous catalysts, some immobilized polymeric catalysts were also developed, e.g. Cu(II)-PS-Im immobilized on silica by quaternization or adsorption [3] and silica-grafted Cu(II)-PS-Im [4]. The goal of this paper is to summarize previous results and to present some additional observations, which support a possible mechanism of the oxidative coupling polymerization of DMP catalyzed by imidazole-based Cu(II) complexes.

7.2 Summary of Previous Experimental Results [1-4]

Under standard conditions without added DMP, EPR spectra of frozen solutions of immobilized or non-immobilized Cu(II) imidazole complexes indicate that the predominant species is a mononuclear $[Cu(imidazole)_4]^{2+}$ complex, which is found to be a more favourable catalyst precursor for higher activity and better specificity for PPO formation than dinuclear complexes. In the absence of initial strong base no dioxygen consumption takes place. A catalytic amount of hydroxide, producing phenolate anions from DMP [5,6], appears to be essential for the start of the reaction. Particularly, with Cu(II)-NMIm or Cu(II)-PS-Im as catalysts, shorter induction times and higher

reaction rates are observed by adding the hydroxide to DMP. On the contrary, much longer induction times and very low reaction rates are obtained when the weaker base triethylamine is used instead of hydroxide (additional result).

When adding base to DMP or to Cu(II) complex, Michaelis-Menten kinetics for DMP are found. For very low $[Cu(II)]_0$ at a constant concentration of polymeric imidazole ligands, a second-order rate dependence on $[Cu(II)]_0$ indicates that dimerization of copper complexes is necessary prior to the re-oxidation of Cu(I) to Cu(II) [7]. The same reaction rates are obtained when either $CuCl_2$ or $Cu(ClO_4)_2$ is used, which seems to confirm that the phenolate anions can also be the bridging ions in the dimerized copper complexes. This is in agreement with a dinuclear structure as proposed by Karlin et al. [8].

For continuous oxidative coupling catalyzed by immobilized Cu(II)-PS-Im, 2,6-di-tert-butylphenol (DTBP) was used as a substrate since it yields only DPQ, which could be continuously detected by UV/VIS spectrophotometry. From these measurements the stability of the catalysts could be derived. Successful application of immobilized polymeric catalysts in a continuous process confirms that phenolate anions, produced from initial hydroxide and DTBP, are regenerated during the oxidative coupling and do not escape from catalytic intermediates. This fact will be taken into account when considering the mechanism of oxidative coupling.

Finally, with Cu(II)-NMIm as catalysts and DMP as substrate, a control experiment carried out in a "stopped flow mixing cell" ($0.5[DMP] = [CuCl_2] = [KOH] = 3.32$ mmol.dm^{-3}; NMIm/Cu=30; toluene/methanol= 13/2 v/v; KOH was added to DMP) indicates that the amount of DPQ formed from totally added DMP is 1.8% (in situ measured by a UV/VIS spectrophotometer at 421 nm; ε=74000 dm^3.mol^{-1}.cm^{-1}). This means that only about 3.6% of the dimer in structure VI of Scheme 1 consists of DPQ or biphenol, the C-C coupled precursor of DPQ, which is quickly oxidized to DPQ even under air atmosphere (Scheme 2) (additional result).

7.3 A Proposed Mechanism

For convenience a schematic representation of the catalytic cycle is given in Scheme 1. The following comments elucidate and support this mechanism (the roman and arabic numerals are corresponding to intermediate complexes and reaction steps in Scheme 1, respectively):

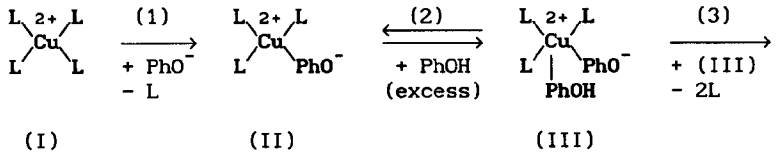
(I) Under standard conditions without added DMP strong EPR signals indicate that the predominant species is mononuclear $[Cu(imidazole)_4]^{2+}$, which

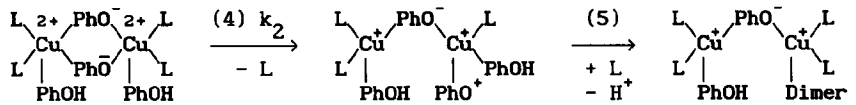
seems to be a favourable catalyst precursor.

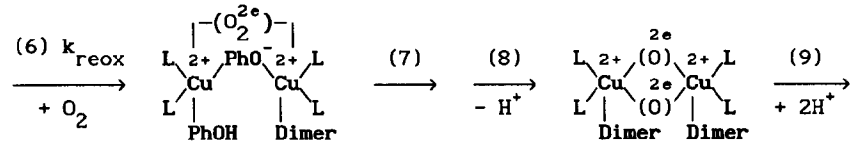
(1) Without addition of catalytic amount of base, no dioxygen consumption takes place; adding base to DMP results in shorter induction time. Stable catalysis of immobilized catalysts in a continuous process confirms that phenolate anions are regenerated during the oxidative coupling and do not escape from the catalytic intermediates.

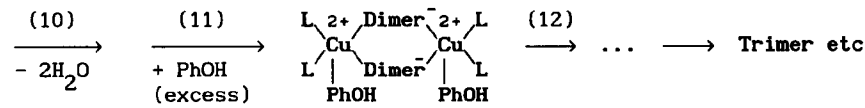
(2) Michaelis-Menten kinetics for DMP are found after adding base to Cu(II) or to DMP.

(3) Reaction rate is proportional to $([Cu(II)]_0)^2$ at very low $[Cu(II)]_0$ for constant [ligand], which indicates that dimerization of copper complexes is necessary prior to re-oxidation [7].









L = N-substituted imidazole ligangs;

Dimer⁻ = Dimer phenolate anions;

PhOH = DMP.

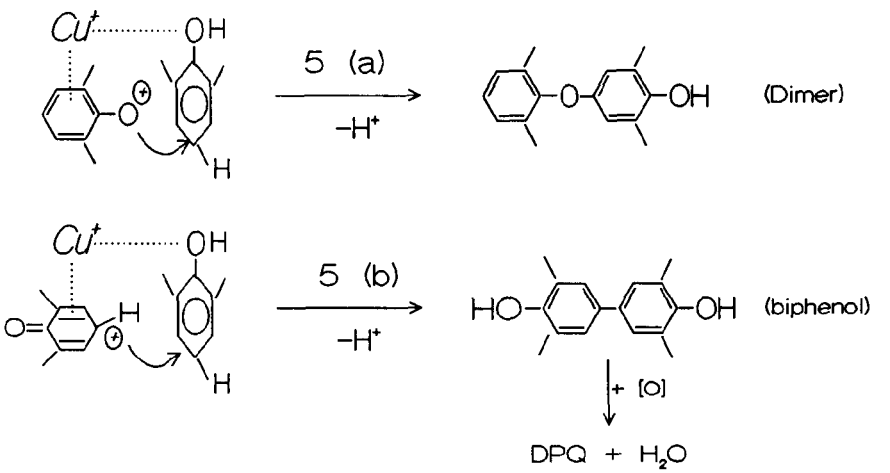
Scheme 1

(IV) Nearly the same reaction rates are found when either $CuCl_2$ or $Cu(ClO_4)_2$ is used. So, PhO^- can be the bridging ion (Cl^- is also a bridging anion, but ClO_4^- is not). Under standard conditions a first-order rate dependence on $[Cu(II)]_0$ is observed, which is correct when only dinuclear complex exists.

(4) This is the rate-determining step: 2Cu(II) (square planar) + PhO^- ⟶ 2Cu(I) (tetrahedral) + PhO^+.

(V) Formation of PhO^+ is preferred to formation of two phenol radicals since now one PhO^- can keep a bridge intact between two Cu(I).

(5) The "side-on" coordinated phenoxonium cation, as described by Uechi et al. for a p-benzoquinone copper complex [9], prefers to attack the para position of a DMP molecule via electrophilic substitution [10] (Scheme 2).



Scheme 2

(a) $PhO^+ + PhOH \xrightarrow{\text{C-O coupling, } -H^+} PhOPhOH$ (Dimer) (PhO^+ in the triplet state [11]).

(b) $PhO^+ + PhOH \xrightarrow{\text{C-C coupling, } -H^+} \xrightarrow{+ [O]} DPQ + H_2O$ (PhO^+ in the singlet state [11]).

(6) This is the re-oxidation step: $2Cu(I) + O_2 \longrightarrow 2Cu(II) + (O_2^{2e})$.

(VII) This structure is in agreement with Karlin's model [8].

(7) $PhO^- + (O_2^{2e}) \longrightarrow PhO^+ + 2(O^{2e})$.

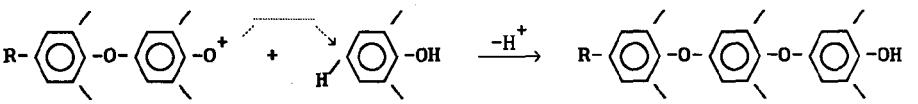
(8) $PhO^+ + PhOH \xrightarrow{\text{C-O coupling, } -H^+}$ Dimer (like (5)).

(9) $2(O^{2e}) + 2H^{+} \longrightarrow 2OH^{-}$.

(10) 2 PhOPhOH + $2OH^{-} \longrightarrow 2PhOPhO^{-} + 2H_2O$.

(11) Still Michaelis-Menten kinetics for DMP.

(12) In following oxidation cycles, dimer (or trimer, etc.) phenolate anions are preferentially oxidized to dimer (or trimer, etc.) phenoxonium cations, wherein some positive charge remains on the oxygen atom in the triplet state [11]. Then the reactions may take place as follows:



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Summary

This thesis describes the immobilization of polymer-bound imidazole Cu(II) complexes on non-porous silica spheres. The catalytic properties of these immobilized polymeric Cu(II) complexes and their non-immobilized polymeric or low-molar-mass analogues were examined in oxidative coupling (polymerization) of 2,6-disubstituted phenols. In view of their intermediate catalytic activity, high specificity and good stability, N-substituted imidazole Cu(II) complexes appear to be promising catalysts for the applied phenol oxidation reactions (**chapter 1**).

In **chapter 2** and **3**, EPR spectroscopic investigations showed that Cu(II) complexes of N-methylimidazole (Cu(II)-NMIm) and poly(styrene-co-N-vinylimidazole) (Cu(II)-PS-Im) have a mononuclear structure $[Cu(imidazole)_4]^{2+}$ in solution for high ligand/Cu ratios. With NMIm a higher ligand/Cu ratio was found to yield an optimum catalyst in the oxidative coupling polymerization of 2,6-dimethylphenol (DMP) with higher catalytic activity and better specificity for the formation of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). A main role of hydroxide as the so-called co-catalyst appears to be to produce the reactive phenolate anion from DMP, which seems essential for the start of the reaction. Michaelis-Menten kinetics in DMP was obtained for the reaction under standard conditions when adding the initial base to Cu(II) complex or to DMP. With the system Cu(II)-NMIm as catalyst at reaction temperatures of 5-25 ^{o}C in toluene/iso-propanol (13/2 v/v), the yield of the side product DPQ (3,5,3',5'-tetramethyl-4,4'-diphenoquinone) was lowered from 3.5% to 0.8-1% by adding the DMP solution slowly to the reaction system. In case of Cu(II)-PS-Im as catalyst, viscometric experiments on solution of polymeric ligands with and without Cu(II) ions showed that the decreasing reaction rate for higher ligand/Cu ratios may be due to overlap of polymer coils. The effect of chain loading α with imidazole ligands on the catalytic activity showed an optimum value for α=0.11, which was explained predominantly in terms of strain in polymer chain segments between neighbouring ligand groups in the same copper complex. The transition of the reaction rate to second order for very low initial Cu(II) concentrations indicates that dimerization of copper complexes is taking place before re-oxidation of Cu(I) to Cu(II). Under standard conditions the identical intrinsic activity (k_2= 0.15 s^{-1}) of Cu(II)-NMIm and Cu(II)-PS-Im measured in three different solvent mixtures, viz. toluene/iso-propanol, toluene/methanol and 1,2-dichlorobenzene (ODCB)/methanol

(13/2 v/v), confirms that the intrinsic catalytic activity of these Cu(II) complexes is mainly determined by the nature of the N-substituted imidazole ligand. However, a better catalytic specificity for PPO formation and a higher molar mass of PPO were obtained in toluene/iso-propanol than in ODCB/methanol. Finally, toluene/methanol appears to be more favourable for a higher K_m^{-1} value (K_m is the Michaelis-Menten constant), which is a measure of the accessibility of active sites for substrate. The smaller overall reaction rates and K_m^{-1} values for Cu(II)-PS-Im than for Cu(II)-NMIm in all cases probably originate from steric hindrance of the polymer backbone and difficult substitution of polydentate ligands by substrate.

Chapter 4 involves immobilization of Cu(II)-PS-Im on modified silica by quaternization, or on unmodified silica by adsorption. These immobilized polymer-bound complexes were applied as catalysts for the oxidative coupling polymerization of DMP in toluene/methanol (13/2 v/v). Higher average chain loading α of PS-Im with imidazole groups, e.g. $\alpha \geq 17\%$, was essential for successful adsorption. A rise in reaction rate was not observed for ligand/Cu>2, which probably resulted from the high viscosity of the silica suspension at high ligand concentration. In a batch process under comparable conditions both types of immobilized polymeric catalysts were found to have the same preference for PPO formation as non-immobilized Cu(II)-PS-im and Cu(II)-NMIm. However, they were five times less active than non-immobilized ones, which was explained primarily in terms of a reduced effective ligand/Cu ratio after the immobilization of polymeric ligands. Application of both types of immobilized polymeric catalysts in a continuously stirred tank reactor (CSTR) for oxidative coupling of 2,6-di-tert-butylphenol (DTBP) was successful. A stable phenol conversion was obtained in CSTR under suitable conditions for at least 120 hours.

An improved immobilization technique for Cu(II)-PS-Im on modified silica was achieved by radical graft copolymerization of N-vinylimidazole (NVIm) and styrene initiated from silica (**chapter 5**). In this graft copolymerization, the same reactivity ratios were found as obtained from non-graft copolymerization initiated by AIBN, i.e. $r_1=0.07$ and $r_2=7.0$ for NVIm and styrene, respectively. In a batch process under comparable conditions, these Cu(II)-PS-Im complexes grafted on silica are catalytically more active for the oxidative coupling of DMP in toluene/methanol (13/2 v/v) than those immobilized on silica by quaternization or adsorption. However, they are still three times less active than non-immobilized Cu(II)-PS-Im or Cu(II)-NMIm for ligand/Cu=4. This is

primarily attributed to a non-optimum complex formation, derived from some theoretical estimations and EPR spectroscopic observations. Decreasing reaction rates for ligand/Cu>4 are probably due to the high viscosities of the silica suspensions. Furthermore, the specificity for PPO formation is not influenced by the grafting of the catalyst for ligand/Cu=4. This silica-grafted Cu(II)-PS-Im also showed a stable conversion under suitable conditions for at least 150 hours in the oxidative coupling of DTBP in a continuous process.

In **chapter 6**, a series of copolymerizations of DMP with 2,2-di(4-hydroxy -3,5-dimethylphenyl)propane (tetramethyl bisphenol-A, TMBPA) catalyzed by Cu(II)-NMIm in toluene/methanol (12/3 v/v) was performed with TMBPA/Cu=1. The main product α,ω-bis(2,6-dimethylphenol)-poly(2,6-dimethyl-1,4-phenylene oxide) (PPO-2OH) was characterized by ^{1}H-NMR spectroscopy and GPC. It consisted of PPO-type telechelics carrying two hydroxyl end groups with $\bar{M}_n$ in the range of 3400-5000 g.mol^{-1} and $\bar{M}_w/\bar{M}_n$ ratios of about 1.5. The formation of side products, i.e. homopolymer PPO and DPQ, could be suppressed by slowly adding the DMP to the reaction system. A likely phenoxonium intermediate mechanism is derived from this copolymerization study.

Finally, **chapter 7** summarizes some experimental results of this study and describes a possible mechanism, via a phenoxonium intermediate, of oxidative coupling of DMP catalyzed by imidazole-based Cu(II) complexes. The main arguments elucidating and supporting this mechanism involve: stable catalysis of immobilized catalysts in a continuous process confirms that phenolate anions are regenerated during the oxidative coupling and do not escape from the catalytic intermediates; nearly the same reaction rates are found when either $CuCl_2$ or $Cu(ClO_4)_2$ is used and so, phenolate anion can be a bridging ion between two copper ions in the dimerized structure; formation of phenoxonium cation is preferred to formation of two phenoxy radicals since now one phenolate anion can keep a bridge intact between two Cu(I). The "side-on" coordinated phenoxonium cation might prefer to attack the para-position of a DMP molecule via electrophilic substitution when some positive charge remains on the oxygen atom of the phenoxonium cation. In this case a PPO dimer is formed instead of DPQ.

Samenvatting

Dit proefschrift beschrijft de immobilisatie van polymeergebonden imidazool Cu(II) complexen op niet-poreuze silica bolletjes. De katalytische eigenschappen van deze geïmmobiliseerde polymere Cu(II) complexen en hun niet-geïmmobiliseerde polymere of laagmoleculaire analoga werden onderzocht bij oxydatieve koppeling(spolymerisatie) van 2,6-digesubstitueerde fenolen. Wegens hun tamelijk goede katalytische activiteit, hoge specificiteit en zeer goede stabiliteit, lijken N-gesubstitueerde imidazool Cu(II) complexen veelbelovende katalysatoren te zijn voor fenol-oxydatie reacties (hoofdstuk 1).

In hoofdstukken 2 en 3 laten EPR-spectroscopische onderzoekingen zien dat Cu(II) complexen van N-methyl-imidazool(Cu(II)-NMIm) en poly(styreen-co-N-vinylimidazool) (Cu(II)-PS-Im) een mononucleaire structuur Cu(imidazool)$_4^{2+}$ hebben in oplossing bij grote ligand/Cu verhoudingen. Een grotere ligand/Cu verhouding leverde een optimale katalysator voor de oxydatieve koppelingspolymerisatie van 2,6-dimethylfenol (DMP) met hogere katalytische activiteit en betere specificiteit voor de vorming van poly(2,6-dimethyl-1,4-fenyleenoxyde) (PPO). Alkalihydroxyde wordt toegevoegd als zogenaamde cokatalysator en heeft als voornaamste rol de vorming van fenolaat anionen uit DMP die essentieel blijken te zijn voor de start van de reactie. Onder standaardkondities werd Michaelis-Menten kinetiek in DMP gevonden na toevoeging van hydroxyde aan het Cu(II)complex of aan DMP. Met Cu(II)-NMIm als katalysator en tolueen/isopropanol (13/2 v/v) als oplosmiddel bij 5-25°C kon de vorming van het ongewenste nevenproduct DPQ (3,5,3',5'-tetramethyl-4,4'-difenochinon) verlaagd worden van 3,5% tot 0,8-1,0% door de DMP oplossing langzaam toe te voegen aan het reactiesysteem. Voor Cu(II)-PS-Im als katalysator kon viscosimetrisch aangetoond worden dat de afnemende reactiesnelheid bij hoge ligand/Cu verhouding mogelijk veroorzaakt wordt door overlap van de polymeerkluwens. De invloed van de beladingsgraad α van de polymeerketens met imidazool-liganden op de katalytische activiteit vertoonde een maximum waarde voor α=0,11, welke verklaard werd op basis van spanning in het ketensegment tussen naburige liganden in het zelfde

kopercomplex. De overgang van de reactiesnelheid naar een tweede orde voor zeer lage Cu(II)-concentraties wijst er op dat dimerisatie van kopercomplexen optreedt voorafgaand aan de reoxydatie van Cu(I) naar Cu(II). Onder standaardkondities werden identieke intrinsieke activiteiten (k_2 = 0,15s^{-1}) gevonden voor zowel Cu(II)-NMIm als Cu(II)-PS-Im in drie verschillende media, n.l. tolueen/isopropanol, tolueen/methanol en 1,2-dichloorbenzeen(ODCB)/methanol (13/2 v/v). Dit bevestigt dat de intrinsieke katalytische activiteit van deze Cu(II) complexen vooral bepaald wordt door de aard van het N-gesubstitueerde imidazool-ligand. Echter in tolueen/isopropanol werd wel een betere specificiteit voor PPO-vorming alsmede een hogere molaire massa van PPO verkregen dan in ODCB/methanol. Tenslotte blijkt tolueen/methanol gunstiger te zijn voor een hogere K_m^{-1}-waarde (K_m is de Michaelis-Menten constante), hetgeen een aanwijzing is voor betere toegankelijkheid van de actieve plaatsen voor het substraat. De lagere reactiesnelheden en K_m^{-1}-waarden voor Cu(II)-PS-Im dan voor Cu(II)-NMIm berusten waarschijnlijk op sterische hindering door de polymeerketen en moeilijke verdringing van polydentaatliganden door substraat.

Hoofdstuk 4 handelt over immobilisatie van Cu(II)-PS-Im door kwaternisering op gemodificeerd silica of door adsorptie op ongemodificeerd silica. Deze geïmmobiliseerde polymeer-gebonden complexen werden toegepast als katalysatoren voor de oxydatieve koppelingspolymerisatie van DMP in tolueen/methanol (13/2 v/v). Hogere gemiddelde beladingsgraden α (α>0,17) van PS-Im met imidazool liganden waren nodig voor succesvolle adsorpties. Voor ligand/Cu>2 werd geen verdere toename in reactiesnelheid waargenomen, hetgeen mogelijk toegeschreven kan worden aan de hoge viscositeit van de silica-suspensie voor hoge ligand-concentraties. In een ladingsgewijs proces vertoonden beide typen geïmmobiliseerde polymere katalysatoren dezelfde voorkeur voor PPO-vorming als de niet-geïmmobiliseerde Cu(II)-PS-Im en Cu(II)-NMIm. Ze waren echter vijf maal minder actief, hetgeen vooral verklaard werd op basis van een verlaagde effectieve ligand/Cu verhouding na immobilisatie van de polymere liganden. Beide typen konden met succes toegepast worden in een continu geroerde tank reactor (CSTR) voor de oxydatieve koppeling van 2,6-di-

tert.butylfenol (DTBP). Onder geschikte kondities werd gedurende tenminste 120 uur een stabiele fenolconversie verkregen.

Radikaal entcopolymerisatie van N-vinylimidazool (NVIm) en styreen geïnitieerd vanaf silica vormde een betere immobilisatietechniek voor Cu(II)-PS-Im op gemodificeerd silica (hoofdstuk 5). Bij deze entcopolymerisatie werden dezelfde reactiviteitsverhoudingen gevonden als voor gewone copolymerisatie geïnitieerd door AIBN, nl. r_1=0,07 en r_2=7,0 voor resp. NVIm en styreen. In een ladingsgewijs proces waren deze op silica geënte Cu(II)-PS-Im complexen actiever bij de oxydatieve koppeling van DMP in tolueen/methanol (13/2 v/v) dan de via kwaternisering of adsorptie geïmmobiliseerde katalysatoren. Echter, ze zijn toch nog drie maal minder actief dan niet-geïmmobiliseerde Cu(II)-PS-Im en Cu(II)-NMIm voor ligand/koper=4. Dit nadeel wordt, op basis van theoretische beschouwingen en EPR-spectroscopische waarnemingen, primair toegeschreven aan niet-optimale complexvorming. De afnemende reactiesnelheden voor ligand/Cu>4 worden waarschijnlijk opnieuw veroorzaakt door hoge viscositeiten van de silicasuspensie. De specificiteit voor PPO-vorming voor ligand/Cu=4 wordt weer niet beïnvloed door enting, terwijl de op silica geënte Cu(II)-PS-Im katalysator gedurende tenminste 150 uur een stabiele DTBP conversie opleverde bij de oxydatieve koppeling in een continu proces.

In hoofdstuk 6 wordt een aantal copolymerisaties beschreven van DMP met 2,2-di(4-hydroxy-3,5-dimethylfenyl)propaan (tetramethyl bisfenol A, TMBPA) gekatalyseerd door Cu(II)-NMIm in tolueen/methanol (12/3 v/v) voor TMBPA/Cu=1. Het hoofdprodukt α,ω-bis(2,6-dimethylfenol)-poly(2,6-dimethyl-1,4-fenyleenoxyde) (PPO-2OH) werd gekarakteriseerd door ^{1}H-NMR en GPC. Het bestond uit PPO-"telechelics" met twee hydroxyl-eindgroepen, $\bar{M}_n$-waarden van 3400-5000 g.mol^{-1} en $\bar{M}_w/\bar{M}_n$ verhoudingen van ca. 1,5. De vorming van nevenprodukten, zoals homopolymeer PPO en DPQ, kon worden onderdrukt door DMP langzaam toe te voegen aan het reactiesysteem.

Tenslotte vermeldt hoofdstuk 7 een samenvatting van enige experimentele resultaten en een daarop gebaseerd mogelijk mechanisme via een fenoxonium intermediair voor oxydatieve koppeling van DMP gekatalyseerd door Cu(II)-imidazool-complexen.

Belangrijke argumenten voor dit mechanisme zijn: stabiele katalyse van geïmmobiliseerde katalysatoren in een continu proces bewijst dat fenolaat anionen geregenereerd worden tijdens oxydatieve koppeling en niet ontsnappen uit de katalytische intermediairen; vrijwel dezelfde reactiesnelheden worden gevonden voor $CuCl_2$ of $Cu(ClO_4)_2$ en dus kunnen fenolaat anionen optreden als bruggende liganden tussen twee koperionen in de gedimeriseerde complexen; de vorming van een fenoxonium kation heeft de voorkeur boven de vorming van twee fenoxy radikalen, omdat dan één fenolaat anion de brug tussen twee Cu(I) ionen intact kan houden. Het "side-on" gecoördineerde fenoxonium kation kan mogelijk bij voorkeur de para-plaats van een DMP molecuul aanvallen via electrofiele substitutie indien enige positieve lading gelokaliseerd blijft op het zuurstofatoom van het fenoxonium kation. In zo'n geval wordt het verlangde PPO-dimeer gevormd in plaats van het ongewenste DPQ.